NMR Methods for Strongly Inhomogeneous Magnetic Fields: Application on Elastomers using the NMR-MOUSE

Von der Fakultät für Mathematik, Informatik und Naturwissenschaften der Rheinisch- Westfälischen Technischen Hochschule Aachen zur Erlangung des akademischen Grades einer Doktorin der Naturwissenschaften genehmigte Dissertation

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Contents

1 Introduction 1

2 NMR Basics 5

3 Measurements of residual dipolar couplings in elastomers containing $^{19}$F 11
   3.1 $^{19}$F Detection by the NMR-MOUSE® ................................. 11
   3.2 Experimental................................................................. 13
      3.2.1 Samples................................................................. 13
      3.2.2 NMR measurements................................................ 13
   3.3 Dipolar couplings in fluorine containing elastomers............... 13
      3.3.1 Transverse relaxation measured with Hahn and solid echoes 13
   3.4 Measurements of dipolar couplings in swollen elastomers........ 18
   3.5 Conclusions...................................................................... 22

4 Multipolar spin states 23
   4.1 Introduction....................................................................... 23
   4.2 Theory............................................................................. 26
      4.2.1 Excitation of dipolar encoded LM and DQ coherences...... 26
      4.2.2 DQ decay curves...................................................... 33
      4.2.3 Dipolar order.......................................................... 36
   4.3 Experimental.................................................................... 40
      4.3.1 Samples................................................................. 40
      4.3.2. NMR Experiments.................................................. 41
4.4 Results and discussion

<table>
<thead>
<tr>
<th>4.4.1 (^1)H dipolar encoded longitudinal magnetization</th>
<th>43</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4.1.1 Natural Rubber</td>
<td>43</td>
</tr>
<tr>
<td>4.4.1.2 Strained elastomers</td>
<td>45</td>
</tr>
<tr>
<td>4.4.1.3 Angular dependence</td>
<td>46</td>
</tr>
<tr>
<td>4.4.1.4 Other Applications</td>
<td>49</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>4.4.2 (^1)H double-quantum build-up curves</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4.2.1 Natural Rubber</td>
<td>50</td>
</tr>
<tr>
<td>4.4.2.2 Strained Elastomers</td>
<td>52</td>
</tr>
<tr>
<td>4.4.2.3 Angular dependence</td>
<td>53</td>
</tr>
<tr>
<td>4.4.2.4 Dipolar encoded LM and DQ coherences for</td>
<td>56</td>
</tr>
<tr>
<td>characterising the spatial distribution of chain</td>
<td></td>
</tr>
<tr>
<td>orientation in stretched elastomers</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>4.4.3 The transverse relaxation of the DQ coherences</th>
<th>58</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>4.4.4 DQ Decay Curves</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4.4.1 Natural rubber</td>
<td>60</td>
</tr>
<tr>
<td>4.4.4.2 Strained Elastomers</td>
<td>63</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>4.4.5 Dipolar order</th>
<th>64</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4.5.1 Natural rubber</td>
<td>64</td>
</tr>
<tr>
<td>4.4.5.2 Strained Elastomers</td>
<td>66</td>
</tr>
</tbody>
</table>

| 4.4.6 Dipolar relaxation time                          | 67 |

| 4.5 Conclusions                                        | 68 |

5 New method for measuring segmental order in elastomers by the accordion magic sandwich

<table>
<thead>
<tr>
<th>5.1 The magic and the mixed echoes</th>
<th>71</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>5.2 The accordion magic sandwich</th>
<th>74</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2.1 Theory</td>
<td>74</td>
</tr>
<tr>
<td>5.2.2 Experimental</td>
<td>78</td>
</tr>
<tr>
<td>5.2.3 Results</td>
<td>78</td>
</tr>
<tr>
<td>5.2.4 Conclusions</td>
<td>81</td>
</tr>
</tbody>
</table>
6 Integral dispersion of rotating frame spin-lattice relaxation time 83

6.1 Spin locking............................................................... 83

6.2 Pulse sequence and theoretical procedure....................... 85

6.3 Experimental................................................................ 86

   6.3.1 Samples.............................................................. 86
   6.3.2 NMR Experiments................................................ 87

6.4 Results........................................................................ 88

   6.4.1 Spin-lock time dependence on volume selection.......... 88
   6.4.2 The influence of the spin-lock field strength on volume
          selection................................................................. 89
   6.4.3 The integrated dispersion of $T_1\rho$ in different cross-linked
          elastomers............................................................. 90
   6.4.4 The integrated dispersion of $T_1\rho$ on strained elastomers... 92
   6.4.5 The anisotropy of $T_1\rho$......................................... 94

7 General conclusions and outlook 97

8 References 101
List of symbols and abbreviations

ADRF  adiabatic demagnetization in the rotating frame
Aflas™ TFE tetrafluoroethylene/propylene copolymer
AIMS accordion magic sandwich
a_m expansion coefficients
B burst propagator describing MS
B_0 static magnetic field vector
B_1 radio-frequency magnetic field in the rotating frame
B_i^{(SL)} amplitude of the spin-locking rf field
B_{eff} effective magnetic field
B_{fic} fictitious magnetic field in the rotating frame
B_{loc} local magnetic field
CPGM Carr-Purcell-Meiboom-Gill
CYCLOPS CYCLically Ordered Phase Sequence
DQ double-quantum
E_m quantum-mechanical energy of state m
ΔE energy difference between neighbouring energy levels
FC 2211 Flourel
FID free induction decay
G_z field gradient in the z direction
\hbar Plank’s constant divided by 2π
H Hamilton operator
\tilde{H}_{d}^{(0)} truncated residual dipolar hamiltonian
H_R the total hamiltonian in the on-resonance rotating reference frame
Hz Hertz
I  nuclear operator
$I_x, I_y, I_z$  components of the spin operator
$\mathbf{J}$  tensor of indirect dipole-dipole coupling
$L$  length of the sample under an uniaxial force
$L_0$  length of the sample in the absence of an force
LM  dipolar encoded longitudinal magnetization
LOSY  Lock selective spectroscopy
$m$  magnetic quantum number
$\mathbf{M}$  magnetization vector
$M_0$  thermodynamic equilibrium magnetization
$M_2, M_4$  second and forth van Vleck moment
MAS  magic angle spinning
MERE  mismatched excitation/reconversion pulse sequence
MOUSE  mobile universal surface explorer
MS  magic sandwich
NMR  nuclear magnetic resonance
NQR  nuclear quadrupolar resonance
NR  natural rubber
$P_2(\cos \theta)$  Legendre polynomial of second order
phr  parts-per-hundred-rubber
$r$  space vector
$rf$  radio-frequency
SBR  styrene-butadiene-rubber
SQ  single-quantum
$\mathbf{T}$  Dyson time ordering operator
$t_1$  evolution time
$T_1$  longitudinal relaxation time
$T_{1p}$  longitudinal relaxation time in the rotating frame
$T_{1\text{peff}}$  effective longitudinal relaxation time in the rotating frame
$T_{1,0}$  irreducible tensor operator of the longitudinal magnetization
$T_{1D}$  relaxation time of the dipolar order
$T_2$  transverse relaxation time
$T_{2^*}$  transverse relaxation in the rotating frame with inhomogeneous broadening
\( T_{2,\pm 2} \) irreducible tensor operator of the double quantum coherence
\( T_{2,0} \) irreducible tensor operator of the dipolar order
\( T_{2,\text{eff}} \) effective transverse relaxation time
\( T_{2\text{DQ}} \) transverse relaxation time of DQ coherence
TBBS benzothiazyl-2-tert-buthyl-sulfenamide
\( T_g \) glass-transition temperature
\( T_{l,p} \) irreducible tensor operator
\( U \) time evolution operator
\( x,y,z \) components of the space vector
\( x', y', z' \) axes for the rotating frame
ZQ zero-quantum
\( \gamma \) gyromagnetic ratio
\( \lambda \) extension ratio
\( \bar{\omega}_d \) preaveraged intragroup dipolar coupling constant in elastomers
\( \omega_d \) angular frequency corresponding to the dipolar local field
\( \omega_{ib} \) angular frequency of the burst pulses
\( \omega_{rf} \) rotation frequency of the rotating frame
\( \omega_0 \) nominal NMR frequency in angular units
\( \sigma \) chemical-shielding tensor
\( \tau_{\text{sl}} \) duration of the spin lock pulse
\( \Theta \) angle between the direction of the applied force and the axis perpendicular to the permanent magnet faces
\( \Theta_m \) magic angle, 54.7°
\( \mu_0 \) magnetic permeability of vacuum
\( \mu \) magnetic moment
\( \rho_{mn} \) density matrix elements
\( \rho \) density operator
\( \tau \) time delay
\( \psi \) wave function
1 Introduction

The standard NMR analytical methods usually implicate the exploitation of large magnets producing homogeneous static fields over the sample volume. Over the last few years low field NMR techniques became more and more crucial because of the large number of applications. Successful applications include NMR logging and geophysical studies [Klei], agricultural purposes [Roll] and medical diagnosis [Fuk], or materials testing with portable NMR surface scanners [Eid], where the sample is situated outside the magnets. The practical advantages of this “in situ” analysis, such as no limitation of the sample size and a non-destructive treatment, are gained at the expense of working in grossly inhomogeneous magnetic fields. In stray-field NMR the sample is intentionally placed in a site where the static magnetic field is very inhomogeneous [McDo]. Using surface coils in NMR Imaging implicates highly non-uniform rf magnetic fields at the sample. Not less significant are the applications of NQR on polycrystalline materials used in the detection of explosives and narcotics [Rud]. In this case, only the component of the rf field along the relevant axis of the electric field gradient tensor is effective, so that the effective rf field varies from crystallite to crystallite.

The NMR-MOUSE® is able to monitor transverse relaxation rates in soft matter, and consequently material properties, which are influenced by molecular motions modulating dipolar couplings [Blü]. It consists of two permanent magnets with anti-parallel magnetization producing the $B_0$ field. The radiofrequency (rf) field is created by a surface coil mounted in between the magnets. The sensitive volume is restricted to regions near the surface of the examined object [Bal]. The given inhomogeneities of $B_0$ and $B_1$ require assessment of the spin system response to the well-known or newly introduced pulse sequences.
The aim of this work is the implementation of new methods for the NMR-MOUSE® to get more understanding about working in strongly inhomogeneous magnetic fields and simultaneously to enlarge its sphere of applications. This is possible either by employing methods established in high field NMR and transforming these for the special conditions of the mobile sensor or by introduction of brand-new methods which are in fact specifically designed for inhomogeneous fields. The final objective then is the correlation of the information obtained with structural and viscoelastic properties of matter. Elastomers are complex macromolecular systems with distributions of correlation times of molecular motions. Based on a cross-linked polymer the properties are determined by many parameters like the monomer unities, cross-linking agents, the presence and homogeneity of the fillers.

The present work is organized as follows: after a brief theoretical general introduction chapters follow which contain four different topics of this work. Every one is treated as an individual theme, with a theoretical, and an experimental part:

1. The first methodical part of this work is the possibility to obtain wideline NMR spectra with the aid of the NMR-MOUSE®. This is studied on fluorinated elastomers using a train of Hahn echoes, to which the system response is encoded by dipolar couplings.

2. A separate question is the feasibility of detecting double-quantum coherences on a cross-linked elastomer sample in the hazardous magnetic fields of the NMR-MOUSE®. After developing suitable pulse sequences and detecting a DQ build-up curve for the first time in inhomogeneous magnetic fields, a new method based on DQ decay curves is developed. The challenge is DQ measurements by the NMR-MOUSE® with improved signal-to-noise ratio. The next step is then to confirm the effect of cross-link density, local strain anisotropy in stretched elastomers on the residual dipolar couplings with the aid of these methods. Behind all this is the concept to establish a new sphere of applications of the NMR-MOUSE®. Multipolar spin states like dipolar order and dipolar encoded longitudinal magnetization, and their detection and application in inhomogeneous magnetic fields are also introduced in this connection.

3. The segmental order in elastomers is investigated by an alternative method, based on determining the residual van Vleck moments for a dipolar network in elastomers, also via residual dipolar couplings. This new method includes the
detection of magic and mixed echoes for the first time by the NMR-MOUSE®, the development the theory to describe the spin system response by using the accordion magic sandwich, and the implementation of these methods in practice for cross-linked elastomers.

4. Measuring spin-lattice relaxation times in the rotating frame with the possibility to characterize slow molecular motions in elastomers is as well a goal of this work.

Developing new methods and adapting pulse sequences, which are established in high field NMR for the special case of the NMR-MOUSE® demands a permanent comparison with similar results in homogeneous, high magnetic fields. In the present report efforts are being made to accomplish this requirement by comparison of the data with the literature results and to mimic the measurements under comparable conditions in high magnetic fields.
2 NMR Basics

A large number of NMR experiments, (for instance, those involving two-dimensional techniques) cannot be described adequately using the classical vector model. The density matrix formalism is the only one with universal applicability. It provides a complete description of the spin system, once its energy levels are fully known (determination of the eigenvalues of the Hamiltonian). We are interested in the time evolution of the density matrix to describe spin system response to various pulse sequences.

Nuclei with spin quantum number \( I > 0 \) have a magnetic moment \( \mu \), which orients in a static magnetic field \( B_0 \) in discrete positions with respect to the main field. This interaction causes the splitting of energy levels. The energy levels \( E_m \) are the eigenvalues of the Zeeman Hamilton operator and are given by

\[
E_m = -\gamma m B_0.
\]  

[2.1]

Here \( m \) is the magnetic quantum number, which assumes the values \(-I \leq m \leq +I\).

The energy difference \( \Delta E \) between neighbouring energy levels determines the NMR frequency \( \omega_0 = 2\pi \nu_0 \),

\[
\Delta E = E_m - E_{m-1} = -\gamma B_0 = h\omega_0
\]

[2.2]

The evolution in time of the wave function of the spin system towards equilibrium is described by the Schrödinger equation:

\[
i \frac{\partial}{\partial t} \left| \psi(t) \right\rangle = \mathbf{H}(t) \left| \psi(t) \right\rangle,
\]

[2.3]

where \( \mathbf{H} \) is the Hamilton operator. The wave function \( \left| \psi(t) \right\rangle \) can be expressed as a superposition of the eigenfunctions \( \left| m \right\rangle \) of the Zeeman Hamilton operator:

\[
\left| \psi \right\rangle = \sum_m a_m(t) \left| m \right\rangle,
\]

[2.4]
with the expansion coefficients $a_m$. At this point we can introduce the density matrix $\rho$ with its elements $\rho_{mn} = \overline{a_m(t)a_n^*(t)}$. It can be shown that this matrix is Hermitian and normalized ($\rho_{mn} = \rho_{nm}^*$ and $\text{Tr}[\rho] = 1$). The equation of motion of the density matrix, known as the von Neumann equation, derives from the Schrödinger equation:

$$i \frac{\partial}{\partial t} \rho = [H, \rho] \tag{2.5}$$

The formal solution of this equation for the density matrix at time $t$ is given by the unitary transformation

$$\rho(t) = U(t, t_0) \rho(t_0) U^{-1}(t, t_0), \tag{2.6}$$

where $U(t) = \exp(-iHt)$ is the time evolution operator. In the case where the Hamiltonian is time-independent (i.e. for the Zeeman interaction of the spins with the static magnetic field), the simplified form of the evolution operator applies

$$U(t) = \exp\{-iHt\}. \tag{2.7}$$

Otherwise, we have to take into account the Dyson time ordering operator $T$, which orders products of time-dependent operators from right to left with increasing time:

$$U(t) = T \exp\left\{ -i \int_0^t H(t') dt' \right\}. \tag{2.8}$$

For short evolution times we can consider the nuclear spins in a good approximation as isolated from the thermal bath. For longer times we have to introduce a relaxation operator, which describes the effects of the lattice on each density-matrix element [Ernst].

### 2.1 Anisotropic Nuclear Spin Interactions

The effective Hamiltonian active in NMR experiments is composed of several components, which describe the diversity of the magnetic and electric interactions contributing to the splitting of the energy levels of the nuclear spin states.

$$H = H_z + H_\sigma + H_r + H_d + H_\rho + H_J. \tag{2.9}$$
Table 2.1 Spin Interactions and Hamiltonians fir $^1$H at 7.4 T [Blü].

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Hamilton Operator</th>
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</thead>
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<tr>
<td><strong>Linear</strong></td>
<td></td>
</tr>
<tr>
<td>Zeeman</td>
<td>$H_z = -\gamma I_z \cdot B_0$</td>
</tr>
<tr>
<td>$rf$</td>
<td>$H_{rf} = -\gamma I_x \cdot B(t)$</td>
</tr>
<tr>
<td>Chemical Shift</td>
<td>$H_\sigma = -\gamma I \cdot \sigma \cdot B_0$</td>
</tr>
<tr>
<td>Gradient</td>
<td>$H_g(t) = -\gamma I \cdot G \cdot r$</td>
</tr>
<tr>
<td><strong>Bilinear</strong></td>
<td></td>
</tr>
<tr>
<td>Dipole-dipole coupling</td>
<td>$H_D = \sum_{k&lt;l} I_k \cdot D_{k,l} \cdot I_l$</td>
</tr>
<tr>
<td>J-Coupling</td>
<td>$H_J = \sum_{k&lt;l} I_k \cdot J_{k,l} \cdot I_l$</td>
</tr>
</tbody>
</table>

The Zeeman interaction

As can be recognized from Table 2.1, the Zeeman interaction is for nuclei with spin $I = 1/2$ the strongest one in NMR. The energy level splitting resulting from $H_z$, defines the NMR frequency $\omega_0$ by [2.2]. The other interactions in Table 2.1 are in high-field-NMR at least three orders of magnitude smaller than Zeeman interaction and can often be treated as a perturbation.

The quadrupole interaction

The quadrupole interaction is only present for nuclei with $I > 1/2$, having a non-spherical distribution of their electrical charge. These nuclei exhibit an electric quadrupole momentum that couples with the electric field gradient from the electrons surrounding the nucleus [Blü]. This interaction is not mentioned in Table 2.1 because the nuclei studied in this work are only non-quadrupolar nuclei.

The interaction with the applied radio-frequency field

The Hamiltonian of the interaction with the rf field has the same form as the Zeeman interaction (cf. Tab. 2.1). The difference is that only the $x$-component of the spin
angular momentum operator \( I \) defines the interaction energy, when the \( B_1 \)-field is applied along the \( x \)-axis of the laboratory coordinate frame. In order to obtain a size of \( H_{rf} \), which dominates all the other interactions leading to a broadening of the spectrum, we have to apply a strong \( B_1 \) field. The length and amplitude of the rf pulses determine the angle of the tilted \( z \)-magnetisation in the rotating reference frame.

**Magnetic Shielding**

The nuclei feel a magnetic field different from the outer \( B_0 \) field. This is because of the shielding effect of the surrounding electrons. The resultant local field is given by:

\[
B = (1 - \sigma)B_0,
\]

where \( \sigma \) is the shielding tensor. The equation for \( H_\sigma \) in Table 2.1 shows, that the shielding is dependent on the strength of the magnetic field \( B_0 \). This shielding is specific of a particular electronic environment and thus of a certain chemical structure.

**Dipole-dipole interaction**

One of the most important interactions is that of a spin with the dipolar field produced by other spins. The dipolar Hamiltonian \( H_D \) (cf. Table 2.1) describes the coupling between a spin and its surrounding partners, where \( I \) and \( \tilde{I} \) are the spin vector operators of the coupling spins. The general dipolar Hamiltonian for \( N \) spins becomes:

\[
H_D = \sum_{k<l} \frac{\mu_B h}{4\pi} \gamma_k \gamma_l \left\{ \frac{I_k \cdot I_l}{|r_k - r_l|^3} - \frac{3[I_k \cdot (r_k - r_l)] 
\cdot [I_l \cdot (r_k - r_l)]}{|r_k - r_l|^5} \right\},
\]

where \((r_k - r_l)\) represents the dipole-dipole distance vector between the nuclei \( k \) and \( l \), and \( |r_k - r_l| \) its length. If the polar angle is described by \( \theta_{kl} \), the truncated form of the dipolar Hamiltonian becomes [Kimm]:

\[
H_{D,\text{trunc}} = \sum_{k<l} \frac{\mu_B h}{4\pi} \gamma_k \gamma_l \frac{(3\cos^2 \theta_{kl} - 1)}{|r_k - r_l|^5} \cdot (3I_k \cdot I_l - I_k I_l).
\]

In heteronuclear spin systems of rare abundance further simplifications can be done due to the weak couplings:

\[
H_{D,IS} = \frac{\mu_B h}{4\pi} \gamma_k \gamma_l \frac{(3\cos^2 \theta_{kl} - 1)}{|r_k - r_l|^5} \cdot I_k \cdot I_l.
\]
The indirect coupling
The direct dipolar couplings are averaged to zero in the case of fast isotropic motions. The remaining bilinear interaction in the liquid state NMR is the so-called J-coupling. It describes the indirect homo- or heteronuclear couplings mediated via the bonding electrons between the respective spins. Although it is the weakest interaction in NMR (1-10 Hz for protons), similar to the chemical shift the J-couplings are fingerprints of the chemical structure [Blü1]. This interaction is not longer considered in this work. An extensive description can be found in [Brau] and [Frie].

Magnetic field gradients and susceptibility
The local $B$-field depends on the homogeneity of the main $B_0$-field. Any local distortion of the magnetic field leads to magnetic field gradients. They are also present at the interface of heterogeneous materials as a result of differences in the magnetic susceptibility.
3 Measurements of residual dipolar couplings in elastomers containing $^{19}\text{F}$

3.1 $^{19}\text{F}$ Detection by the NMR-MOUSE®

$^{19}\text{F}$ NMR is increasingly being used because of its high sensitivity (83% of the sensitivity of protons) [Eva]. The high gyromagnetic ratio of $^{19}\text{F}$ gives rise to strong dipolar interactions, which can be exploited to determine structural parameters. The dipolar interactions of $^{19}\text{F}$ reach out much further into the distance compared to $^{13}\text{C}$. Furthermore, the broad chemical shift range of $^{19}\text{F}$ (up to 400 ppm) provides very good chemical resolution, and usually no natural abundance background has to be considered in biological systems [Gra1]. The van der Waals radius of fluorine (1.4 Å) is very similar to that of hydrogen (1.2 Å), although electronegativity effects have to be considered. The strong dipolar interactions together with the chemical shift anisotropy often lead to broad lines in solids, which is a severe problem for the acquisition of high-resolution spectra. The heteronuclear ($^{1}\text{H}$-$^{19}\text{F}$) dipolar coupling can be suppressed by high-power $^{1}\text{H}$-decoupling. $^{19}\text{F}$ high-resolution solid state experiments with heteronuclear $^{1}\text{H}$-decoupling have successfully been performed by Miller et al. [Mill]. Both the feasibility of suppressing the $^{19}\text{F}$ chemical shift in static experiments on a high-field spectrometer and of resolving $^{19}\text{F}$-$^{19}\text{F}$ dipolar interactions even without heteronuclear $^{1}\text{H}$-decoupling was shown in the literature [Har]. The homonuclear $^{19}\text{F}$-$^{19}\text{F}$ dipolar coupling can be averaged by multipulse techniques or by high-speed MAS [Har].

In the case of the NMR-MOUSE® the possibility of detecting $^{19}\text{F}$ nuclei is thus almost self-evident. This was done at 18.9 MHz with the NMR-MOUSE®, which works at 20.1 MHz for protons. The problem is, that because of the magnetic field inhomogeneities, it is difficult to detect selectively the $^{19}\text{F}$ signal. By selecting a reduced volume of the sample one can be certain to detect the $^{19}\text{F}$ nuclei without $^{1}\text{H}$ signals from lower depths. The solution is to use a sample with the following size: 1.5
mm thick, 2 mm wide and 10 mm long, positioned on the coil along the x direction exactly in the middle of the gap in between the magnets. Figure 3.1 illustrates both the static and rf magnetic field distributions and the sensitive volume excited by the NMR-MOUSE® [Gut1]. By choosing the above mentioned sample geometry it is possible to reduce the frequency range of the excited nuclei and in this way to filter out the pure $^{19}$F NMR signal.

![Fig. 3.1](image)

**Fig. 3.1** The NMR-MOUSE® consists of two permanent magnets with anti-parallel magnetization, producing the $B_0$ field. For rf irradiation a surface coil is mounted in between the magnets. a) The geometry of the $B_0$ field as a function of the location $z$ across the gap and the distance $y$ from the surface, represented by isosurfaces crossing the axis of the rf coil at 3 mm. The magnetic field was computed as a Coulombian field by using the surface charge approximation [Bal]. b) The $B_1$ rf field component orthogonal to $B_0$ as a function of $z$ and $y$. c) Sensitive volume of the NMR-MOUSE® calculated for a Hahn echo with the frequency tuned to an average measurement depth of 3 mm.
3.2 Experimental

3.2.1 Samples

The fluoroelastomer analyzed in this chapter is a product of the company Dyneon, with the commercial name Aflas™ TFE. It consists of an alternating tetrafluoroethylene/propylene dipolymer (–CF₂-CF₂-CH(CH₃)-CH₂–). Aflas TFE elastomers are used for wire and cable primary insulation and jacketing as well as for connectors, insulating boots and other applications because of its excellent electrical resistance properties combined with high temperature (250°C) and chemical resistance.

The second fluoroelastomer, which was analysed is Fluorel (FC 2211), a copolymer of vinylidene fluoride and hexafluoropropylene (–CH₂-CF₂-CF(CF₃)-CF₂–) from the company Dyneon, with a fluorine content of 66%.

3.2.2 NMR measurements

The ¹H and ¹⁹F measurements were done at 20.1 MHz and 18.9 MHz, respectively. The recycling delay was 0.5 s, the pulse length 2.5 µs (10 dB attenuation), 400 scans were used for the Hahn echo measurements, and 2000 scans for the multipulse sequences.

3.3 Dipolar couplings in fluorine containing elastomers

3.3.1 Transverse relaxation measured with Hahn and solid echo

The Hahn [Hahn] and solid echo [Mans] experiments start with the spins being in thermal equilibrium. The first pulse excites the spins coherently and generates appropriate single quantum spin coherences. In the next interval the coherences are dephased by distributions of the spin interactions. There are two ways of spin manipulation: a) changing the phases of the spin states by one or more rf pulses, so that coherences lagging behind are promoted and coherences advancing ahead are placed backwards, and b) reversing the sign of the Hamiltonian responsible for dephasing of the coherences, so that the coherences evolve backwards. After the
refocusing interval the spin echo arises and the spin coherences are reestablished. If the coherences are of the single quantum type, an echo signal can be acquired.

On the time scale of the experiment, it is possible to refocus the linear spin interactions (chemical shift, field inhomogeneities). The refocusing efficiency depends on the flip angle of the refocusing pulse (Fig. 3.2). For a flip angle of the second rf pulse adjusted to 180° the initial coherences are fully refocused, for a 90° flip angle half of the initial transverse magnetization is recovered [Kimm]. The static dipolar couplings of two spins (bilinear spin interactions) are fully refocused by a 90° refocusing pulse (solid echo). In the case of a pulse flip angle of 180° the bilinear homonuclear dipolar couplings are not refocused and modulate the decay of the NMR signal (Hahn echo). The effective dipolar coupling as manifested in the linewidth of the spectrum gives a measure of molecular mobility.

The amplitude of the Hahn echo as a function of the echo time ($2\tau$) is used to measure the transverse relaxation $T_2$:

$$a_{\text{Hahn}}(2\tau) = M_0 \exp \left( -\frac{2\tau}{T_2} \right)$$  \[3.1\]

The time constant which describe the decay of the solid echo amplitude is referred to as $T_{2e}$. In the solid state $T_{2e}$ can be different from $T_2$ and because of the refocusing of the dipolar interactions it is often longer than $T_2$.

In the case of the NMR-MOUSE® there is a distribution of flip angles. It is difficult to measure a pure Hahn or solid echo, so that the differences on the values of $T_2$ resp. $T_{2e}$ for solid samples are not well defined. Nevertheless, it was shown using the NMR-MOUSE®, that for different cross-linked SBR elastomer samples the transverse relaxation time measured by Hahn and solid echoes have different values [Gut2].
We measured the transverse magnetization for two different fluoroelastomers, the Fluorel (vinylidene fluoride/hexafluoropropylene dipolymer \(-\text{CH}_2\text{-CF}_2\text{-CF}\left(\text{CF}_3\right)\text{-CF}_2-\)) and Aflas (tetrafluoroethylene/propylene dipolymer \(-\text{CF}_2\text{-CF}_2\text{-CH}\left(\text{CH}_3\right)\text{-CH}_2-\)) by the NMR-MOUSE\textsuperscript{®} at a Larmor frequency of 20.1 MHz for protons and 18.9 MHz for \(^{19}\text{F}\). For both elastomers we obtained different values of \(T_2\) and \(T_{2e}\) by \(^1\text{H}\) and \(^{19}\text{F}\) measurements (see Table 3.1). In the case of Aflas the decay of the transverse relaxation is very fast (30 µs) and thus the signal is highly distorted by the background signal of the NMR-MOUSE\textsuperscript{®}. A partition of the background contribution to the signal was done by subtracting the echo amplitudes measured under the same conditions by the NMR-MOUSE\textsuperscript{®} without any sample (Table 3.1).
Measurements of residual dipolar couplings in elastomers containing $^{19}$F

Fig. 3.3 $^{19}$F Hahn and solid echo decays from Fluorel recorded with the NMR-MOUSE® at 18.9 MHz by incrementing the echo time $\tau$ (see Fig. 3.2).

Table 3.2 Transverse relaxation of fluoroelastomers recorded by the NMR-MOUSE® at the frequency of 20.1 MHz for $^1$H and 18.9 MHz for $^{19}$F using a Hahn echo and a solid echo pulse sequence (Fig. 3.2).

<table>
<thead>
<tr>
<th>Transverse relaxation</th>
<th>Fluorel $^{19}$F</th>
<th>Aflas $^{19}$F</th>
<th>Aflas $^1$H</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_2$ (Hahn decay)</td>
<td>0.06 ms</td>
<td>0.03 ms</td>
<td>0.03 ms</td>
</tr>
<tr>
<td>$T_{2e}$ (solid decay)</td>
<td>0.08 ms</td>
<td>0.04 ms</td>
<td>0.04 ms</td>
</tr>
</tbody>
</table>

The evolution of magnetization under the influence of homonuclear couplings is unaffected by the rf pulses generating the Hahn echo, while the phase evolution resulting from different chemical shifts, heteronuclear couplings, and magnetic field inhomogeneities is reversed [Blü]. Thus the echo amplitude is modulated by the homonuclear dipolar couplings. The Fourier transform of the decay of the echo maxima results in a narrow line with a width determined by the $T_2$ relaxation.

The pure dipolar spectrum of a rotating CH$_3$-group consists of a triplet with relative intensities 1:2:1, like an axially symmetric, quadrupolar spectrum of a nucleus with spin $I = \frac{3}{2}$ [Mos]. The positions of the outer lines depend on the angle between the C-CH$_3$ axis and the static magnetic field direction according to the second
Legendre polynomial \( \left(3 \cos^2 \theta - 1\right)/2 \), similar to the doublet arising from two coupled spins \( I = \frac{1}{2} \) [Gra1].

The Aflas polymer sample contains two magnetically equivalent \(^{19}\text{F}\) nuclei, coupled by a strong dipolar interaction (CF\(_2\)). The \(^{19}\text{F}\)-NMR Hahn echo powder spectrum may look like a Pake doublet. But it is dominated by magnetic field inhomogeneities in the case of the NMR-MOUSE\(^\circledR\) (Fig. 3.4) and the chemical shift anisotropy in highly homogeneous magnetic fields (see Fig. 3.5), and further broadened by multi-center homo- and heteronuclear dipolar couplings. The relatively strong \(^{19}\text{F}\) dipolar couplings between different functional groups (CF\(_2\)) makes it difficult to detect the Pake doublet even in homogeneous high magnetic fields. The \(^{1}\text{H}\) Hahn echo spectra are represented by a broad line and do not provide any information about the structure of the fluoropolymers. In all the spectra the maxima of the echoes were recorded and Fourier transformed. The spectra of the NMR-MOUSE\(^\circledR\) were recorded after subtracting the background signal intensity. For strongly fluorinated systems the strong homonuclear dipolar coupling requires high-speed MAS to resolve the fluorine lines according to their chemical shifts. Heteronuclear dipolar couplings between protons and fluorines also contribute to the linewidth in the proton dimension.

**Fig. 3.4** The \(^{1}\text{H}\) (a) and \(^{19}\text{F}\) (b) Hahn echo NMR spectrum of Aflas TFE measured by the NMR-MOUSE at a Larmor frequency of 20.1 MHz and 18.9 MHz, respectively. The Fourier transformation of the maximum of the Hahn echo amplitude is recorded by incrementing the echo time \( \tau \) (Fig. 3.2a) with an increment of 10 \( \mu \text{s} \).
3.4 Measurements of dipolar couplings in swollen elastomers

Pake did the earliest NMR experiment for studying structure in the solid state by spectroscopy. The dipolar interaction of two protons of water molecules in gypsum shows a Pake doublet spectrum, where the frequency splitting is a direct determination of the distance between the protons [Pak]. More recently, it was shown, that using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence [Carr, Meib] one obtains exactly the same information as from the FID that would occur if only the like spin interactions exist. Such a type of experiment have been used to obtain pure homonuclear dipolar $^{19}$F spectra of a CF$_3$ group, by suppressing the chemical shift anisotropy, the heteronuclear dipolar couplings, and field inhomogeneities [Gra2]. A powder line shape was obtained with three peaks for the CF$_3$ groups in a non-oriented sample, like for a quadrupolar spin with $I = \frac{3}{2}$.

In order to isolate the CF$_2$- and CH$_3$- groups by the solvent molecules, the Aflas fluoroelastomer was swollen in acetone-D$_6$. We acquired the Hahn echo and multipulse CPMG spectra. These measurements were not possible with the NMR-MOUSE$^\text{®}$ on the crude Aflas polymer because the relaxation time $T_2$ was too short. The line width of the resonance narrows with increasing levels of swelling (lower

---

1 This measurement was performed by Dr. Marco Bertmer
cross-linking levels) because of the increasing amplitude and frequency of chain
motions in the same time. The interstitial domain geometry and the magnitude of the
susceptibility differences between bulk solvent and swollen polymer domains are a
function of swelling. In Figure 3.6a and 3.6b the $^{19}$F Hahn echo and CPMG spectra of
the swollen Aflas fluoroelastomer acquired with the NMR-MOUSE® at 18.9 MHz are
shown. The line narrowing is effectively identifiable compared to the unswollen
polymer (Fig. 3.4a), but no splitting was observed. One reason for that could be the
proton dipolar couplings. Another important reasons are the magnetic field
inhomogeneities and the fact that the molecular motion of the CF$_2$ groups is now
faster, so that the homonuclear $^{19}$F-$^{19}$F dipolar couplings are more averaged out.
Swelling the elastomer is a good solution to facilitate the measurements by the NMR-
MOUSE®, but the direct consequence is that the detection of dipolar interactions
becomes more complicated. On the other hand the difference in the magnetic
susceptibility between the internal pores and the polymer bulk give rise to magnetic
susceptibility artifacts. Possibly, they do not matter in the highly inhomogeneous
fields of the MOUSE. The $^1$H spectra of the swollen fluoroelastomer in Figure 3.7 a
and b lead to similar results, the dipolar couplings are not strong enough to be
detectable by the NMR-MOUSE® in such circumstances.

![Fig. 3.6](image)

**Fig. 3.6** a) The $^{19}$F single-pulse Hahn echo NMR spectrum of Aflas TFE measured by
the NMR-MOUSE® at 18.9 MHz. The Fourier transform of the maximum of the Hahn
echo amplitude by incrementing the echo time $\tau$ (Fig. 3.2a) was recorded. b) The $^{19}$F
multipulse CPMG NMR spectrum of Aflas TFE measured by the NMR-MOUSE® at
18.9 MHz. The Fourier transformation of the maximum of the echo amplitude by
incrementing the echo time $\tau$ is recorded. The measurements were done with a
CPMG pulse sequence in analogy to that in Figure 3.5, but with pulse phase $\gamma$ of the
refocusing pulses.
Fig. 3.7 a) The $^1$H single-pulse Hahn echo NMR spectrum of Aflas measured by the NMR-MOUSE® at 20.1 MHz. The Fourier transformation of the maximum of the Hahn echo amplitude by incrementing the echo time $\tau$ (Fig. 3.2a) is recorded. b) The $^1$H multipulse CPMG NMR spectrum of Aflas measured by the NMR-MOUSE® at 20.1 MHz. The Fourier transformation of the maximum of the echo amplitude by incrementing the echo time $\tau$ is recorded. The measurements were done with a CPMG pulse sequence analogue those in the Figure 3.8, but with the pulse phase $y$ of the refocusing pulse.

Exact $\pi$ pulses refocus interactions linear in the spin coordinate (chemical shift, heteronuclear spin dipole-dipole) but do not affect the (bilinear) like-spin dipole coupling. Incomplete refocusing due to pulse imperfections in the CPMG pulse sequence leads to the accumulation of errors. These errors give rise to a loss in echo amplitude, and can be compensated by phase cycling schemes [Liz]. We used in addition to the primary CPMG pulse sequence, the $xy8$ phase cycle with the cycle length $\tau_c = 16\tau$ (Fig. 3.8) and sampled the data in every window between successive $\pi$ pulses to increase the spectral width. Figure 3.9 shows the $^{19}$F spectrum measured with the aid of the CPMG pulse sequence with an $xy8$ phase cycling by the NMR-MOUSE®. The spectrum could not be resolved because of the appearance of artifacts. In the $xy8$ case, even though the errors in the echo amplitude do not accumulate like in the original CPMG sequence, they are repeated after every cycle. This leads to “sidebands” in the spectrum at frequencies $\pm \frac{1}{\tau_c}, \pm \frac{2}{\tau_c}, \text{etc}$. The $^1$H spectra presented in Figure 3.10 a and b confirm the presence of these artifacts, particularly in the spectrum of the natural rubber sample, where no resolved dipolar interactions are supposed to be observed. An appropriate phase cycle scheme and an adequate selection of $\tau$ was not helpful to get rid of the artifacts. It was already
shown by simulations, that this pulse sequence does not work in inhomogenous magnetic fields [Bal].

Fig. 3.8 The CPMG pulse sequence with an xyθ phase cycling used to extract the dipolar interaction. The 90° and 180° flip angle correspond θ and 2θ for the NMR-MOUSE® because of the flip angle distribution.

Fig. 3.9 The 19F multipulse CPMG NMR spectrum with the xyθ phase cycle of Aflas TFE measured by the NMR-MOUSE® at 18.9 MHz. The Fourier transform of the maximum of the echo amplitude by incrementing the echo time τ (increment factor 0.2 ms) was recorded.

Fig. 3.10 a) The 1H multipulse CPMG NMR spectrum with the xyθ phase cycle of Aflas TFE measured by the NMR-MOUSE® at 20.1 MHz. The Fourier transform of the maximum of the echo amplitude by incrementing the echo time τ (increment factor 0.2 ms) is recorded. b) The equivalent spectrum of a natural rubber sample.
3.5 Conclusions

The strong dipolar couplings present in $^{19}$F containing polymers are advantageous because they can be exploited to determine specific structural parameters. The main reason that $^{19}$F NMR has not yet found a more widespread application seems to be technical one: The need for high-power $^1$H decoupling at a frequency close to that of $^{19}$F, together with a wide chemical shift range at high magnetic field strength, put demands on filtering, probe design and spectrometer hardware [Car]. Nevertheless, the feasibility of resolving $^{19}$F-$^{19}$F dipolar interactions even without heteronuclear $^1$H decoupling and of suppressing the $^{19}$F chemical shift anisotropy in a static experiment was shown [Gra1]. In the low, inhomogeneous magnetic fields of the NMR-MOUSE® it would be more suitable to choose an oriented sample containing isolated spin pairs of $^{19}$F nuclei and no protons, like stretched elastomers or fibers. In this case the dipolar couplings are more pronounced but at the same time the $T_2$ times are very short and difficult to record with the NMR-MOUSE®. A new NMR-MOUSE® with much shorter or without any background signal, or the possibility of proton decoupling would be a desirable improvement.
4 Multipolar spin states

4.1 Introduction
In this chapter we investigate the possibility to excite multipolar spin states in strongly inhomogeneous fields using the NMR-MOUSE®. These multipolar spin states or spin modes correspond mainly to longitudinal magnetization (LM) or polarization, multiple-quantum (MQ) NMR coherences and spin order [Bow1, Bow2] (and refs. therein). The dipolar and quadrupolar states are conveniently described, especially for the last case, by the irreducible tensor operators $T_{l,p}$ of rank $l$ and order $p$ (see, for instance [Bow1]). For a dipolar coupled spin-1/2 pair or a quadrupolar nuclei with spin $I=1$, the irreducible tensor operators $T_{1,0}$, $T_{2,±2}$ and $T_{2,0}$ correspond to longitudinal magnetization, double-quantum (DQ) coherences and dipolar order (DO), respectively.

Why spin multipolar states? In pulsed NMR, it is advantageous to have a physical picture of the status of the nuclear ensemble, at any given instant of time. The tensor operators transform under rotations of the coordinate system, in the same manner as spherical harmonics [Hal]. This feature can be used therefore, to produce polar representations of nuclear ordered states. The dipole and quadrupolar states for nuclei with $I=1$ are represented in Fig. 4.1. However these polar diagrams are not wave functions, but rather representations of the various multipolar states of the nuclear ensemble. To obtain equivalent diagrams in terms of magnetization vectors, we have to insert straight lines linking negative to positive lobes. In this way we obtain a graphical representation of the multipolar states, as shown in Fig. 4.2. From these diagrams it is now easy to imagine how a $T_{2,2}(a)$ nuclear state can be produced, starting from a $T_{2,1}(a)$ state: by applying a nonselective $\pi/2$ pulse about the $x'$ axis. In addition, we note that second rank $T_{2,p}(s,a)$ multipolar states can never generate conventional NMR signals because their net magnetization is equal to zero (for the detailed description of the irreducible, spherical tensor operators see for
example [Ernst]). The suffices \((s)\) and \((a)\) refer to the symmetric and antisymmetric combinations, respectively, of the \(T_{l,0}\) tensor operators.

\[
\begin{align*}
T_{1,0} & , T_{2,0} \\
-T_{1,1}(a) & , iT_{1,1}(s) \\
-T_{2,1}(a) & , iT_{2,1}(s) \\
-iT_{2,2}(a) & , T_{2,2}(s)
\end{align*}
\]

**Fig. 4.11** Polar representations of the \(T_{l,p}(s,a)\) nuclear ordered states for \(I = 1\) nuclear ensembles.

\[
\begin{align*}
T_{1,0} & , T_{2,0} \\
-T_{1,1}(a) & , iT_{1,1}(s) \\
-T_{2,1}(a) & , iT_{2,1}(s) \\
-iT_{2,2}(a) & , T_{2,2}(s)
\end{align*}
\]

**Fig. 4.12** Magnetic vector representations of the \(T_{l,p}(s,a)\) nuclear ordered states for \(I = 1\) nuclear ensembles.
Recently, it was shown that for dipolar coupled spins the multipolar LM state is encoded by the dipolar interactions [Schn1]. A spin multipolar state, which is not present for quadrupolar nuclei is the zero-quantum coherence (ZQ). Nevertheless, for isolated spin-1/2 pairs with different chemical shifts the selective excitation of one resonance can convert DQ coherences into ZQ coherences [Karls]. For obvious reasons, in a strongly inhomogeneous magnetic field this procedure cannot be applied. In a dipolar multi-spin network the pulse sequences used for excitation of DQ coherences will also excite ZQ coherences and dipolar encoded LM. The response of the LM, ZQ and DO (dipolar order state) to the phase cycling of rf pulses is the same making the separation of these states difficult. Nevertheless, in general, the life times of DQ and ZQ coherences are very different from that of dipolar encoded LM and DO which is related to the spin-lattice relaxation times $T_1$ and $T_{1D}$, respectively. These features can be used together with other procedures for filtering these multipolar spin states.

A new method is discussed theoretically and proved experimentally which allows for measuring DQ decay curves having as a starting point a maximum value of the excited DQ coherences. This procedure was also tested employing a solid-state superconducting NMR spectrometer using different pulse tilt angles, which partially mimics the field inhomogeneities present for the NMR-MOUSE®. This method leads to an improved accuracy in the measurements of the ratio of total residual dipolar couplings. The experiments were conducted on natural rubber samples with different cross-link densities showing the sensitivity of the DQ build-up and decay curves to cross-link density. The possibility to measure quantitatively the ratio of $^1$H total residual dipolar couplings from DQ decay curves recorded by the NMR-MOUSE® is also discussed.

We have to mention that in strongly inhomogeneous fields the existence of a broad flip-angle distribution of rf pulses precludes the implementation of some filtration experiments. Fortunately, there are experiments, which work in the presence of strong field inhomogeneities. The Jeener-Broekaert experiment [Jeen] producing multipolar states of dipolar or quadrupolar order does not relay upon the flip-angle effect to suppress the unwanted signal components [Kemp1, Kemp2, Brow]. The required discrimination arises as a result of the nominal 90° pulse and the first nominal 45° pulse having orthogonal phases. This phase condition can be fulfilled for all the voxels in the sample in the presence of strongly inhomogeneous fields.
Moreover, the rf pulse phases are well defined over the sensitive volume and enable one to use well-established phase cycling procedures [Ernst, Mun] for filtering DQ coherences and dipolar encoded longitudinal magnetization.

4.2 Theory

4.2.1 Excitation of dipolar encoded LM and DQ coherences

Multi-quantum coherences are off-diagonal elements of the density matrix, which arise in systems with spin $I > \frac{1}{2}$ and in systems of coupled spins. The multi-quantum transitions are those, in which more than one spin flip simultaneously. For example in the case of double quantum coherences both spins flip in the same direction and for the zero-quantum transition they flip in opposite directions (for more details see [Blü]).

The simplest method to excite and detect MQ coherences exploits a time reversal procedure like the nonselective three-pulse sequence [Ernst, Mun] or its variant presented in Fig. 4.3. Here the durations of excitation and reconversion periods are equal and the efficiency in pumping MQ coherences is increasing in the initial excitation/reconversion time regime. A build-up curve is recorded in this case, for which a maximum is present as a result of the competitive effects of pumping MQ coherences and transverse relaxation of single-quantum coherences [Schn1].

We shall consider in the following the spin system response to the pulse sequence of Fig. 4.3b used for excitation of MQ coherences [Wies1]. The case of a rigid, magnetically equivalent, isolated two spin-1/2 system will be treated excited by radio-frequency pulses having well defined arbitrary flip angles. This will give us the possibility to investigate the multipolar spin states which can be excited by the NMR-MOUSE®, i.e. in strongly inhomogeneous magnetic fields where a distribution of pulse flip angles exist. Nevertheless, the radio-frequency pulse phases are not distributed over the sample volume. They are the same for each voxel.
Fig. 4.13 (a) General scheme for filtering NMR signals according to dipolar encoded LM and MQ coherences. This scheme is similar to a two dimensional MQ experiment but it is used with fixed evolution time $t_1$ and variable, but equal, excitation/reconversion times $\tau$. (b) A five-pulse sequence with an arbitrary pulse flip angle $\theta$, supplemented by $2\theta$ pulses to measure dipolar encoded LM and DQ filtered signals with variable excitation/reconversion times. The evolution time $t_1$ is kept short and constant and a $2\theta$ pulse is applied at the middle of this interval for partially refocusing the DQ coherence evolution under inhomogeneous Hamiltonians. This pulse is applied in the middle of the $t_1$ interval in alternative scans for dipolar encoded LM experiments. The $z$ filter is represented by the last $\theta$ pulse of the reconversion period and a free evolution period of duration $\tau_0$. The detection in strongly inhomogeneous magnetic fields is achieved by a Hahn echo. The phase cycling schemes used in the experiments are listed in Tables 4.1 and 4.2.
Table 4.3  Basic phase cycling scheme used for recording dipolar encoded LM. Additionally, the CYCLOPS scheme was employed, yielding a 32-step phase cycle. The rf pulses Pi (i = 1 - 9) correspond to those of Fig. 4.3b. The $2\theta$ pulse in the middle of the evolution period was switched on and off between successive phase cycle steps.

<table>
<thead>
<tr>
<th>radio-frequency pulse and receiver phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
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<tr>
<td>P2</td>
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<td>P3</td>
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<td>P4</td>
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<td>P7</td>
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<td>P8</td>
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<tr>
<td>P9</td>
</tr>
<tr>
<td>receiver</td>
</tr>
</tbody>
</table>

Table 4.4  Basic phase cycling scheme used for recording DQ filtered signals. Additionally, the CYCLOPS scheme was employed, yielding a 16-step phase cycle. The rf pulses Pi (i = 1 - 9) correspond to those in Fig. 4.3b. In this experiment a $2\theta$ pulse (pulse P4) was applied in the middle of the evolution period.

<table>
<thead>
<tr>
<th>radio-frequency pulse and receiver phases</th>
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<tbody>
<tr>
<td>P1</td>
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<td>P2</td>
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<td>P9</td>
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<tr>
<td>receiver</td>
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</table>
The spin system response for an isolated, magnetically equivalent two spin-1/2 system can be described by an equivalent quadrupolar nucleus with spin I=1 (see for instance [Kimm]). Under the action of the pulse sequence presented in Figure 4.3b the reduced density operator $\sigma$ can conveniently be described at various moments of times in terms of the irreducible tensor operators $T_{l,p}$. In a system of coupled spins, the rank $l$ indicates the number of spins correlated, while the order $p$ indicates the quantum number of the respective coherence. Transitions between different ranks of the tensor occur under the action of the dipolar Hamiltonian while rotations induced by the rf pulses lead to transitions between linear combinations of tensors having the same rank but different orders [Ernst]. A rotation of the density operator is achieved by the application of rf pulses. Thus a combination of pulses and evolution delays is necessary to create DQ coherences.

In our case the effect of partial refocusing by $2\theta$ rf pulses (cf. Fig. 4.3b) will be neglected in the following being not essential for the filtration of DQ coherences. Nevertheless, these pulses refocus the fast coherence decay of inhomogeneous nature, being essential for the success of the experiment. The experiment starts with the spin system exhibiting $z$ polarization, i.e. $\sigma(0^-) \propto T_{1,0}$. After the action of the first hard $\theta_x$ pulse, the spin density develops to

$$\sigma(0^-) \propto T_{1,0} \cos \theta + iT_{1,1}(s) \sin \theta,$$

where $T_{1,1}(s)$ is the symmetric irreducible tensor operator of $T_{1,z1}$ representing the transverse magnetization, defined as $iT_{1,1}(s) = \frac{1}{\sqrt{2}}[T_{1,1} + T_{1,-1}]$ [Bow1].

At the end of the first free evolution period of duration $\tau$ (cf. Fig 3b), under the effect of the truncated residual dipolar Hamiltonian $\tilde{H}_{d}^{(o)} = \tilde{\omega}_d T_{2,0}$, where $\tilde{\omega}_d$ is the preaveraged intragroup dipolar coupling constant in elastomers [Coh] the density operator is given by

$$\sigma(\tau^-) \propto T_{1,0} \cos \theta + iT_{1,1}(s) \cos \left( \sqrt{\frac{3}{2}} \tilde{\omega}_d \tau \right) \sin \theta$$

$$+ \sqrt{2} T_{2,1}(a) \sin \left( \frac{3}{2} \tilde{\omega}_d \tau \right) \sin \theta$$

[4.2]
where the antisymmetric combination of the irreducible tensor operators $T_{2,\pm 1}$ is given by $T_{2,\pm 1}(a) = -\frac{1}{\sqrt{2}}[T_{2,1} - T_{2,-1}]$, [Bow1]. $T_{1,0}$ commutes with the Hamiltonian, so that the $T_{1,0}$ term is unchanged. In Eq. [4.2] all the relaxation processes have been neglected.

The second rf $\theta_x$ pulse (cf. Fig. 4.3b) transforms the density operator to:

$$\sigma(\tau^+) \propto T_{1,0} \cos^2 \theta - T_{1,0} \sin^2 \theta \cos \left( \frac{3}{2} \Omega_D \tau \right)$$

$$\quad + \frac{1}{2} T_{1,1}(s) \sin 2\theta + \frac{1}{2} T_{1,1}(s) \sin 2\theta \cos \left( \frac{3}{2} \Omega_D \tau \right) \quad . \quad [4.3]$$

$$\quad + \sqrt{2} T_{2,1}(a) \cos^2 \theta \sin \left( \frac{3}{2} \Omega_D \tau \right) + \frac{1}{2} T_{2,2}(a) \sin 2\theta \sin \left( \frac{3}{2} \Omega_D \tau \right)$$

Therefore, at the end of the excitation period dipolar encoded and non-encoded longitudinal magnetization ($T_{1,0}$), dipolar encoded and non-encoded single-quantum coherences ($T_{1,1}(s)$), dipolar encoded antiphase single-quantum coherences ($T_{2,1}(a)$), and dipolar encoded double-quantum coherences ($T_{2,2}(a)$) have been excited. The operator $T_{2,2}(a)$ indicates a simultaneous transition of a coupled spin pair. It is also evident that no dipolar order or zero-quantum coherences are present. This fact is also valid for DO in the case of dipolar coupled multi-spin systems or quadrupolar nuclei with $I>1$. Nevertheless, based on the selection rules valid for MQ NMR spectroscopy [Ernst, Mun, Ba, Tyc] ZQ coherences are excited by the nonselective three pulse sequence for a dipolar network with the number of spins $N>2$.

LM and DQ multipolar spin states [Wies2] can be filtered from the other coherences and from each other by specific phase cycling schemes (see below). From Eq. [4.3] the density operators describing LM and DQ multipolar spin states are given at the end of the excitation period by

$$\sigma_{LM}(\tau^+) \propto T_{1,0} \cos^2 \theta - T_{1,0} \sin^2 \theta \cos \left( \frac{3}{2} \Omega_D \tau \right), \quad [4.4]$$

and

$$\sigma_{DQ}(\tau^+) \propto i \sqrt{2} T_{2,2}(a) \sin^2 \theta \sin \left( \frac{3}{2} \Omega_D \tau \right), \quad [4.5]$$

respectively.
The MQ coherences are acquired indirectly as single quantum coherences because they are not detectable directly. Therefore the double quantum has to be converted into transverse magnetization again. This is realized by the reversion of the excitation Hamiltonian that can be interpreted as reversing the time in the propagator. Once the evolution of LM and DQ multipolar spin states during the $t_1$ period is neglected the density matrix after the first $\theta_y$ reconversion pulse is given by

$$\sigma_{LM}(\tau^+ + t_1^+) \propto [T_{1,0} \cos \theta - T_{1,1}(a) \sin \theta] \left[ \cos^2 \theta - \sin^2 \theta \cos \left( \frac{3}{2} \omega_D \tau \right) \right]$$ \hspace{1cm} [4.6]$$

and

$$\sigma_{DQ}(\tau^+ + t_1^+) \propto i\sqrt{2} \left[ - T_{2,1}(s) \sin \theta + T_{2,2}(a) \cos \theta \right] \sin^2 \theta \sin \left( \frac{3}{2} \omega_D \tau \right)$$ \hspace{1cm} [4.7]$$

Let’s consider again the action of the truncated residual dipolar Hamiltonian

$$\overline{H}_q^{(0)} = \overline{\omega}_q T_{2,0},$$ of the length $\tau$ for the reconversion. Since $T_{1,0}$ and $T_{2,2}$ commute with the dipolar Hamiltonian, the density matrices become

$$\sigma_{LM}(2\tau + t_1) \propto \left\{ T_{1,0} \cos \theta + \left[ T_{1,1}(a) \cos \left( \frac{3}{2} \omega_D \tau \right) - i\sqrt{2} T_{2,1}(s) \sin \left( \frac{3}{2} \omega_D \tau \right) \right] \sin \theta \right\}$$

$$\cdot \left[ \cos^2 \theta - \sin^2 \theta \cos \left( \frac{3}{2} \omega_D \tau \right) \right]$$ \hspace{1cm} [4.8]$$

and

$$\sigma_{DQ}(2\tau + t_1) \propto \left\{ -i\sqrt{2} T_{2,1}(s) \cos \left( \frac{3}{2} \omega_D \tau \right) - \frac{i}{ \sqrt{2} } T_{1,1}(a) \sin \left( \frac{3}{2} \omega_D \tau \right) \right\} \sin \theta + i\sqrt{2} T_{2,2}(a) \cos \theta$$

$$\cdot \sin^2 \theta \sin \left( \frac{3}{2} \omega_D \tau \right).$$ \hspace{1cm} [4.9]$$

Let’s observe now just the $T_{1,0}$ and $T_{1,1}$ terms, because $I_z = T_{1,0}$, $I_y = i T_{1,1}(s)$, and $I_x = -T_{1,1}(a)$, respectively. We apply the last $\theta_y$ pulse of the reconversion. The LM and the DQ density operator then have the simplified forms:

$$\sigma_{LM}(2\tau^+ + t_1^+) \propto \left\{ T_{1,0} \cos^2 \theta + T_{1,1}(a) \sin \theta \cos \theta$$

$$- T_{1,0} \sin^2 \theta \cos \left( \frac{3}{2} \omega_D \tau \right) + T_{1,1}(a) \sin \theta \cos \theta \cos \left( \frac{3}{2} \omega_D \tau \right) \right\}$$

$$\cdot \left[ \cos^2 \theta - \sin^2 \theta \cos \left( \frac{3}{2} \omega_D \tau \right) \right]$$ \hspace{1cm} [4.10]$$
and

\[ \sigma_{DQ}(2\tau^* + t_1) \propto \left( T_{1,0} \sin \theta - T_{1,1}(a) \cos \theta \right) \sin^3 \theta \sin^2 \left( \frac{3}{2} \omega_d \tau \right). \] \[ \text{[4.11]} \]

At the end of the filter of duration \( \tau_0 \) (cf. Fig. 4.3) the LM and DQ encoded \( z \)-polarizations correspond to the \( T_{1,0} \) term. Finally the LM and DQ filtered normalized signals originating from a \( \theta \) voxel are given by

\[ \frac{S_{\theta}}{S_0} \left( \tau_0 + 2\tau \right) \propto \cos^4 \theta + \sin^4 \theta \left( \cos \left( \frac{3}{2} \omega_d \tau \right) \right), \] \[ \text{[4.12]} \]

and

\[ \frac{S_{\theta}}{S_0} \left( \tau_0 + 2\tau \right) \propto \sin^4 \theta \left( \sin^2 \left( \frac{3}{2} \omega_d \tau \right) \right), \] \[ \text{[4.13]} \]

respectively. In Eqs. [4.12] and [4.13] the evolution of LM and DQ multipolar spin states during the \( t_1 \) period was neglected and \( S_0 \) is the SQ signal detected by a Hahn echo with a short echo time. In the derivation of the eq. [4.12] \( \left( \cos \left( \frac{3}{2} \omega_d \tau \right) \right) \) is zero because the integral is zero as a consequence of the distribution of the orientation of the end-to-end vector in the polymer network. Furthermore, the relaxation of coherences characterized by an effective relaxation time \( T_{2,\text{eff}} \) during excitation and reconversion periods can be neglected for \( \tau < T_{2,\text{eff}} \). The symbol \( \left( \ldots \right) \) represents the averages taken over the orientation of the spin-pair internuclear vectors and the statistics of the end-to-end vectors [Schn1]. Equations [4.12] and [4.13] describe the signals originating from a particular sample voxel characterized by an rf pulse having a \( \theta \) flip angle for the NMR-MOUSE\textsuperscript{®}. The total, filtered signals can be evaluated as in [Bal], and the relevant part is given by an integral that includes \textit{inter alia} the space distribution of the flip angles. This integral can be evaluated numerically from a given distribution of the static and radio-frequency fields [Bal] and is expressed by the symbol \( \left( \ldots \right)_\theta \). From Eqs. [4.12] and [4.13] one finally gets:

\[ \frac{S_{LM}(\tau_0 + 2\tau)}{S_0} \propto \left( \cos^4 \theta \right)_\theta + \left( \sin^4 \theta \right)_\theta \left( \cos^2 \left( \frac{3}{2} \omega_d \tau \right) \right), \] \[ \text{[4.14]} \]

and
If the excitation/reconversion intervals $\tau$ fulfill the conditions $\bar{\omega}_0 \tau \ll 1$, and $\tau \ll T_{2,\text{eff}}$ the above equations can be approximated by

$$\frac{S_{\text{DQ}}(\tau_0 + 2\tau)}{S_0} \propto \left\langle \sin^4 \theta \right\rangle_\theta \left\langle \sin^2 \left( \frac{3}{2} \bar{\omega}_0 \tau \right) \right\rangle.$$

[4.15]

The derivative of the LM decay curve and DQ build-up curve taken over the variable $\tau^2$ in this initial time regime yields a quantity related to the square of the total (inter- and intra-functional groups) residual dipolar couplings of the elastomer segments.

For a multi-spin dipolar topology the effect of pumping DQ high-order spin correlations and high-order MQ coherences leads to a more complex treatment than that described above. Nevertheless, the above equations are expected to be valid in the regime of short excitation/reconversion times [Schn1].

### 4.2.2 DQ decay curves

The new feature of this method is related to the possibility to generate MQ coherence decay curves, which can be adjusted to begin with a maximum MQ signal. This will allow for a more accurate determination of the residual dipolar couplings with the NMR-MOUSE® compared to the method employing MQ build-up curves (cf. Fig. 4.3), because of the much better signal to noise ratio at the maximum of the curve. The spin system response to the mismatched excitation/reconversion pulse sequence (MERE) (see Fig. 4.4) used for excitation and detection of MQ coherences gives a DQ decay curve by incrementing the time delay $\tau^*$ and setting the parameter $\tau$ to the maximum of the DQ build-up curves [Wies1].
Fig. 4.14: (a) Schematic representation of the experiment for mismatched excitation and reconversion of MQ coherences used for recording decay curves. The excitation time $\tau$ and the evolution time $t_1$ are kept fixed and only the mismatched reconversion time $\tau'$ is varied. The parameter $\tau$ is set to the maximum of the DQ build-up curves. (b) A five-pulse sequence with an arbitrary flip angle $\theta$, supplemented by $2\theta$ partially refocusing pulses for measuring DQ-filtered coherence decay curves. The evolution time $t_1$ is kept short and constant and a $2\theta$ pulse is applied at the middle of this interval for partially refocusing the coherence evolution under inhomogeneous Hamiltonians.

The case of a two spin-1/2 system is treated in the presence of homogeneous magnetic fields for which well defined arbitrary pulse flip angles can be defined all over the sample volume. This gives us the possibility to understand how the MERE pulse sequence works for the NMR-MOUSE®, i.e. in strongly inhomogeneous magnetic fields where a distribution of pulse flip angles exist. Nevertheless, the radio-frequency pulse phases are the same for each sample voxel.

Under the action of the pulse sequence presented in Figure 4.4b the reduced density operator $\sigma$ and the DQ encoded $z$-polarization at the end of the reconversion period and the $z$-filter of duration $\tau_0$ (cf. Fig. 4.4b) can be evaluated as in chapter 1.2.1, where the matched variant is described. In eq. [4.15] if we replace the reconversion time $\tau$ by the time $\tau + \tau'$ (compare Figs. 4.3 and 4.4) the DQ filtered signal after the $z$-filter is finally given by

$$S_{DQ}(\tau_0 + 2\tau + \tau') \propto \left\langle \sin\left(\frac{3}{2} \omega_0 (\tau + \tau')\right) \sin\left(\frac{3}{2} \omega_0 \tau\right) \right\rangle \sin^4 \theta,$$  \[4.18\] where the evolution of DQ coherences during the $t_1$ period has been neglected. The symbol $\langle \ldots \rangle$ represents the averages taken over the orientation of the spin-pair.
internuclear vectors and the statistics of the end-to-end vector [Gra, Schn1]. In the case of the NMR-MOUSE® eq. [4.18] describes the signal originating from a particular sample voxel characterized by an rf pulse having a flip angle $\theta$. For an rf pulse flip angle of $\theta = 90^\circ$ and matched excitation/reconversion pulse sequence, i.e. $\tau = 0$, Eq. [4.18] becomes identical with the DQ signal derived for a static collection of spin-1/2 pairs [Schn1]. For a $\tau$ parameter which has a value in the region of the maximum of the DQ build-up curve, i.e., for $\left(\sin^2\left(\frac{\theta}{2}\right)\right) = 1$ and $\left(\cos\left(\frac{\theta}{2}\right)\right) = 0$ we can approximate Eq. [4.18] by

$$S_{DQ}(\tau_0 + 2\tau + \tau') \propto \left< \cos\left(\frac{\theta}{2}\right)\right> \sin^4 \theta.$$

[4.19]

If the $\tau'$ interval fulfills the conditions $\omega_d\tau'<<1$, and $\tau'<<T_{2,\text{eff}}$ we can write eq. [4.19] as follows:

$$S_{DQ}(\tau') \propto \left(1 - \frac{3}{4} \left< \omega_d^2 \right> \tau'^2\right) \sin^4 \theta.$$

[4.20]

In the presence of transverse relaxation of single-quantum coherences during excitation and reconversion periods Eq. [4.20] has to be multiplied by the function $\exp[-(2\tau + \tau')/T_{2,\text{eff}}]$ where $T_{2,\text{eff}}$ is the effective transverse relaxation time.

$$S_{DQ}(\tau') \propto \left(1 - \frac{3}{4} \left< \omega_d^2 \right> \tau'^2\right) \exp[-2\tau/T_{2,\text{eff}}] \sin^4 \theta.$$

[4.21]

We note that this approximation is not necessary for the evaluation of DQ build-up curves [Schn1]. Nevertheless, the values of the residual dipolar couplings measured by the DQ build-up and decay curves are in a good agreement as it is shown below. Finally, the normalized DQ filtered signal is given by

$$\frac{S_{DQ}(\tau')}{S_{DQ}(0)} \propto \left(1 - \frac{3}{4} \left< \omega_d^2 \right> \tau'^2\right) \sin^4 \theta.$$

[4.22]

i.e., the signal represents a DQ decay curve starting from an initial time $\tau' = 0$, after pumping DQ coherences for a duration $\tau$. The slope of the DQ decay curve with regard to $\tau'^2$ gives a quantity related to the total residual dipolar couplings of the elastomer segments. The sensitivity to the residual dipolar couplings can be defined as a derivative of the curve slope versus $\left< \omega_d^2 \right>$. For the DQ decay curves this...
derivative is $3/4$, being two times lower as compared to the DQ build-up curves (eq. [4.17]) [Wies1].

For a multi-spin dipolar topology the effect of pumping DQ high-order spin correlations and multiple-quantum coherences leads to a more complex treatment as that described above. Nevertheless, Eq. [4.22] is expected to be still valid in the limit of small values of $\tau^{-1}$ (see chapter 4.4 results and discussion).

### 4.2.3 Dipolar order

In addition to the energies of coupling of each spin species with the large external field (Zeeman energies), there is a quasi-invariant of the motion the spin-spin or dipolar coupling energy, which plays an essential role in many processes. The degree of dipolar order (dipolar energy) in a nuclear spin system in complete thermal equilibrium with the lattice is very small, because the local fields, which are the cause of the dipolar ordering are mostly only a few gauss. An essential step in most experiments on the properties of dipolar energy is thus the transformation of the easily available Zeeman order into observable amounts of dipolar order. The methods originally proposed were the adiabatic demagnetization in the laboratory frame or in the rotating frame (ADRF) are not suitable for the study of fast phenomena, such as very fast spin-lattice relaxation of the dipolar energy, because they transfer spin order slowly, in times much longer than the spin-spin relaxation times [Jeen]. An alternative fast method is the Jeener-Broekaert pulse sequence, consisting of two rf pulses, $\pi/2$ out of phase with one other and separated by a time of the order of $T_2$. The disadvantage of this method is that it can convert the Zeeman order only to about 58% in dipolar order.

Let's consider the following experiment: a sample with a long $T_1$, which has been polarized in a high field is slowly removed from the field [And]. Outside the large field there is no magnetization in the sample (short $T_2$). If the sample is now reintroduced into the magnetic field at the same rate as it was removed and the total duration of the experiment is short compared with $T_1$, almost all magnetization present at the beginning of the experiment will reappear in a time short compared to $T_1$. The explanation of this is the following: the sample was removed adiabatically from the field, the entropy did not change. Therefore the initial ordering along the field was preserved in another form when it was in low field. In fact, in each small region of
the sample the magnetization becomes aligned along the local field at that point. This spin order is called dipolar order. The time constant for the exponential decay due to dissipation of dipolar order to the thermal bath along each of the local field vectors is $T_{1D}$, the dipolar relaxation time. Since the local fields are oriented randomly, there is no net magnetization to observe. When the sample is reintroduced in the field isentropically the ordering appears again as Zeeman order [Fuku].

The excitation of the DO multipolar spin state can be achieved by the Jeener-Broekaert pulse sequence [Jeen]. This pulse sequence was adapted to the NMR-MOUSE® sensor. The scheme is similar to that used for excitation of LM and MQ multipolar spin states and possesses preparation (sample polarization), excitation, evolution and reconversion periods (cf. Fig. 4.5a).

Fig. 4.15 (a) General scheme for recording dipolar order build-up curves based on the Jeener-Broekaert experiment [Jeen]. The evolution time $t_1$ is kept fixed and only the excitation/reconversion time $\tau$ is varied. (b) Jeener-Broekaert three-pulse sequence with arbitrary flip angles $\theta$ and $\theta/2$, supplemented by $2\theta$ pulses for partial refocusing. The evolution time $t_1$ is kept constant and long enough so that DQ and ZQ coherences will irreversibly be dephased. A $2\theta$ pulse (represented by a gray area) is applied in alternative scans at the middle of the $t_1$ interval for partially filtering of the LM spin state. The amplitude of the dipolar echo is detected. The phase cycle employed is listed in Table 4.3.
Table 5 Basic phase cycling scheme used for recording the DO multipolar spin state. Additionally, the CYCLOPS scheme was employed, yielding a 32-step phase cycle. The rf pulses Pi (i = 1 - 6) correspond to those of Fig. 4.5b.

<table>
<thead>
<tr>
<th>radio-frequency pulse and receiver phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
</tr>
<tr>
<td>P2</td>
</tr>
<tr>
<td>P3</td>
</tr>
<tr>
<td>P4</td>
</tr>
<tr>
<td>P5</td>
</tr>
<tr>
<td>P6</td>
</tr>
</tbody>
</table>
receiver  | y | y | -x | -x | -y | -y | x | x |

The spin system response to the action of the pulse sequence of Fig. 4.5b can be evaluated under the same conditions as discussed in the previous section. Using the eqs. [4.1], and [4.2] for the evolution of irreducible tensor operators under the first rf pulse and dipolar interaction, we can write for the density operator at the end of the excitation period after the $\theta/2_y$ rf pulse

$$
\sigma(\tau) \propto T_{1,0} \cos(\theta/2) \cos \theta + T_{1,1}(a) \sin(\theta/2) \cos \theta \\
+ i T_{1,1}(s) \sin \theta \cos \left( \frac{3}{2} \omega_d \tau \right) \\
- \sqrt{2} \left[ \frac{\sqrt{3}}{2} T_{2,0} \sin \theta - T_{2,1}(a) \cos \theta - \frac{1}{2} T_{2,2}(s) \sin \theta \right] \sin \theta \sin \left( \frac{3}{2} \omega_d \tau \right).
$$  \[4.23\]

It is evident that multipolar spin states of LM, SQ, DQ and dipolar order (DO) are produced. The irreducible spin operator $T_{2,0}$ describes the last spin state. If the evolution period $t_1$ is longer than the transverse relaxation times of SQ and DQ coherences only the LM (or Zeeman order), which now is not encoded by the dipolar interaction, and the DO will survive. After the evolution time eq. [4.23] becomes:

$$
\sigma(\tau + t_1) \propto T_{1,0} \cos(\theta/2) \cos \theta - \sqrt{3} T_{2,0} \sin^2 \theta \sin \left( \frac{3}{2} \omega_d \tau \right).
$$  \[4.24\]

The $\theta$ pulse applied in the middle of the evolution period (cf. Fig. 4.5b) will change the sign of the LM allowing a partial filtering of this spin state (see below). We apply now the second $\theta/2_y$ rf pulse
\[ \sigma(\tau + t_1^*) \propto T_{1,0} \cos^2(\theta/2) \cos \theta + \frac{1}{2} T_{1,1}(a) \sin \theta \cos \theta \]
\[ - \sqrt{\frac{3}{2}} \left[ \frac{1}{4} T_{2,0} \left(1 + 3 \cos \theta\right) + \frac{\sqrt{3}}{2} T_{2,1}(a) \sin \theta + \frac{\sqrt{3}}{4} T_{2,2}(s) \left(1 - \cos \theta\right) \right] \sin^2 \theta \sin \left( \sqrt{\frac{3}{2}} \bar{\omega}_D \tau \right) \]

[4.25]

Like in a Jeener-Broekaert experiment [Jeen] performed with 45° pulses, the signal detected in phase with the last \( \theta/2 \) pulse after the action of \( \bar{H}_d^{(0)} = \bar{\omega}_D T_{2,0} \) is encoded only by the DO.

\[ \sigma(2\tau + t_1) \propto \frac{1}{2} T_{1,1}(a) \sin \theta \cos \theta \cos \left( \sqrt{\frac{3}{2}} \bar{\omega}_D \tau \right) + \frac{3}{4} T_{1,1}(s) \sin^3 \theta \sin^2 \left( \sqrt{\frac{3}{2}} \bar{\omega}_D \tau \right). \]

[4.26]

In eq. [4.26] we took only the components contributing to the signal into account. Since \( I_y = iT_{1,1}(s) \), resp. \( I_x = -T_{1,1}(a) \), the normalized spin state of DO detected at the maximum of the transferred dipolar echo is given by

\[ \frac{S_{DO,y}(2\tau)}{S_0} \propto \frac{3}{4} \left( \sin^3 \theta \right)_0 \left( \sin^2 \left( \sqrt{\frac{3}{2}} \bar{\omega}_D \tau \right) \right). \]

[4.27]

The equation above is valid only for small \( t_1 \) values when the spin-lattice relaxation of the dipolar order can be neglected. For the case of spin-1/2 pairs the dipolar encoding of DQ coherence and DO is the same (cf. Eqs. [4.15] and [4.27]), but the flip angle encoding is different. Therefore, as for the DQ case a DO build-up curve can be recorded when the excitation/reconversion time \( \tau \) is incremented. In the initial excitation regime from Eq. [4.27] the NMR signal filtered for DO is given by

\[ \frac{S_{DO,y}(2\tau)}{S_0} \propto \frac{9}{8} \left( \sin^3 \theta \right)_0 \left( \bar{\omega}_D \right)^2 \tau^2, \]

[4.28]

when the transverse relaxation of coherences during the excitation and reconversion period is neglected.

We can mention here that the DO build-up curves which can be recorded by the changes in the excitation/reconversion time \( \tau \) (cf. Fig. 4.5a) are not limited to spin-1/2 pairs or quadrupolar nuclei with spin \( I=1 \). This effect can be also detected for a dipolar-coupled multi-spin network as is evident from the results of Jeener and Broekaert [Jeen]. The inverse spin temperature associated with the dipolar reservoir reaches a maximum when \( \left| \frac{d}{d\tau} G(\tau) \right| \) is maximum, where the function \( G(\tau) \) describes the free induction decay.
4.3 Experimental

4.3.1 Samples

A series of cross-linked elastomer samples based on commercially available natural rubber (NR) SMR10 (Malaysia) was investigated. The additives were 3 phr (parts-per-hundred-rubber) ZnO and 2 phr stearic acid. The sulfur and accelerator contents are 1-1 phr for the sample NR1 and 5-5 phr for NR5. The accelerator is of the standard sulfenamide type (TBBS, benzothiazyl-2-tert-butyl-sulfenamide). After mixing the compounds in a laboratory mixer at 50°C, the samples were vulcanized at 160°C in a Monsanto MDR-2000-E vulcameter. The degree of cross-linking was measured by the low frequency shear modulus at a temperature of 160°C in the vulcameter directly after the vulcanization. The measurements were performed with oscillation amplitude of ±0.5° and a frequency of 1.67 Hz.

Table 4.6 Cross-link series of natural rubber.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sulphur-accelerator content (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR1</td>
<td>1-1</td>
</tr>
<tr>
<td>NR2</td>
<td>2-2</td>
</tr>
<tr>
<td>NR3</td>
<td>3-3</td>
</tr>
<tr>
<td>NR4</td>
<td>4-4</td>
</tr>
<tr>
<td>NR5</td>
<td>5-5</td>
</tr>
</tbody>
</table>

For the experiments performed under mechanical stress a simple home build stretching device was used. The natural rubber bands had the dimensions of 180 mm x 35 mm x 4 mm in the unstrained state. The NMR-MOUSE® was positioned below the rubber band in contact with the surface of the rubber band (Fig. 4.6). The width of the band was larger than the diameter of the radio-frequency coil of 13 mm.
The investigated Styrene-Butadiene-Rubber (SBR) is based on the commercially available SBR 1500 composed of 23.4 weight % styrene units and 76.6 weight % butadiene units distributed in a random sequence. The samples contain 3 phr (parts-per-hundred-rubber) ZnO and 2 phr stearic acid. The sulfur and accelerator contents are 1-1 phr for the sample SBR1, 3-3 phr for the sample SBR3, and 5-5 phr for SBR5. After mixing the compounds in a laboratory mixer at 50 °C, the samples were vulcanized at 160 °C in a Monsanto MDR-2000-E vulcameter. The degree of cross-linking was measured by the low frequency shear modulus at a temperature of 160 °C in the vulcameter directly after the vulcanization.

**4.3.2. NMR Experiments**

The $^1$H NMR experiments in inhomogeneous fields were performed with a home-made NMR-MOUSE® sensor equipped with a Bruker Minispec spectrometer operating at a carrier frequency of 20.1 MHz and a coil geometry with a sensitive volume of about 9 mm x 4 mm in plane and 0.5 mm in depth. Further details are published in ref. [Eid]. The length of a pulse employed in all the measurements had a value of 2.5 μs, the z-filter time was $\tau_0 = 500$ μs, and the Hahn echo time was $\tau_1 = 100$ μs (cf. Figs. 3b and 4b). The evolution time was $\tau_e = 60$ μs, $\tau_i = 100$ μs, and $\tau_{e1} = 60$ μs for DQ, DO, and LM experiments, respectively. The DQ decay curves were
recorded using the MERE pulse sequence [Wies1] with a fixed value of $\tau = 1$ ms, and $\tau = 0.8$ ms corresponding to the maximum of the DQ build-up curves for the sample NR1 for two extension ratios $\lambda = 1.00$ and $\lambda = 2.25$, respectively. The intensity of the DQ filtered signals for two different excitation/reconversion times $\tau = 0.5$ ms and $\tau = 1.6$ ms taken around the value of $\tau$ corresponding to the maximum of the build-up curve was measured for the NR1 band with $\lambda = 2.5$ versus the angle $\Theta$ between the direction perpendicular to the magnet poles and the direction of the stretching force. This measurements can easily be performed with the NMR-MOUSE® sensor.

The NMR experiments in homogeneous fields were performed at a $^1$H frequency of 500.045 MHz on a Bruker DSX-500 solid-state spectrometer. The 90° pulse length was 2 $\mu$s. To partially mimic the effect of rf pulse inhomogeneities the LM and DO filtered signals were recorded with an rf pulse flip angle of about $\theta = 60^\circ$. The same pulse delays were used as for the measurements performed with the NMR-MOUSE®. The acquisition was performed without employing a Hahn echo. By applying $2\theta$ pulses in the middle of the excitation, evolution, and reconversion periods (cf. Figs. 3b and 4b and the discussion below) partial refocusing of the signal was achieved.

Phase cycling schemes for detecting dipolar-encoded LM [Schn1, Schn2], DQ coherences [Ernst, Mun] and DO [Kemp1, Kemp2] filtered signals were applied in all experiments. The basic phase cycles without CYCLOPS are presented in Tables 4.1 to 4.3. In the DQ experiments ZQ coherences (and also LM) are filtered out by the classical phase cycle [Ernst, Mun]. For the experiment concerning the multipolar LM state the difference of the filtered signals recorded with and without the $2\theta$ refocusing pulse was taken. The refocusing pulse will not change the sign of the ZQ and DQ coherences. Because ZQ coherence, dipolar encoded LM and DO behave in the same way under the phase cycle of the rf pulses the elimination of ZQ and DQ coherences in LM experiments could also be achieved by choosing the $t_1$ evolution period longer than the longest value of $T_{2,ZQ}$, and $T_{2,DQ}$ relaxation times. The inhomogeneities of the static magnetic field only nearly affect the lifetime of the ZQ coherence [Ernst]. In the experiments for excitation of DO the orthogonality of the phases of the first $\theta$ pulse and the $\theta/2$ pulse (cf. Fig. 4.5b) allows the excitation of the MQ coherences of odd order for the spin system starting from z polarization [Ba, Tyc]. Therefore, ZQ coherence will not be excited in this case. The single-quantum
and MQ coherences of higher order (i.e., $|p| \geq 3$) are filtered out by the combined effect of phase cycle and fast dephasing during the $t_1$ period. Partial filtration of LM is achieved by the $2\theta$ radio-frequency pulse applied in the middle of the evolution period which is switched on and off between successive scans (cf. Table 4.3).

4.4 Results and discussion

4.4.1 $^1$H dipolar encoded longitudinal magnetization

4.4.1.1 Natural Rubber

The possibility to measure signals filtered by $^1$H dipolar encoded LM using the NMR-MOUSE® and the pulse sequence presented in Fig. 4.3 is demonstrated by the LM decay curves recorded on the two natural rubber samples NR1 and NR5. These curves are shown in Fig. 4.7 for the full relevant range of the excitation/reconversion times. In the initial regime of the excitation/reconversion times the decay is dominated by a $\tau^2$ dependence as revealed by eq. [4.16]. This is supported by the dipolar encoded LM decay curves shown in the inset of Fig. 4.7. Moreover, the effect of transverse relaxation of the SQ coherences during excitation and reconversion periods is not present being linear in $\tau$ for the initial time regime. The signal-to-noise ratio is relatively good making it possible to quantitatively evaluate residual dipolar couplings.
Fig. 4.17: $^1$H normalized dipolar encoded LM decay curves for the natural rubber samples NR1 ($\Delta$) and NR5 (•) which differ in cross-link density. The decay curves have been recorded with the NMR-MOUSE® using the pulse sequence of Fig. 4.3b and the phase cycle of Table 4.1. The dipolar encoded LM signals were normalized to the intensity of the Hahn echo recorded with the same echo time as that used for the decay curves. The inset shows the linear dependence on $\tau^2$ (solid lines) for the decay curves in the initial excitation/reconversion regime.

Fig. 4.18: $^1$H normalized dipolar encoded LM decay curves for the natural rubber samples NR1 ($\Delta$) and NR5 (•) with different cross-link densities measured using a solid-state Bruker DSX 500 NMR spectrometer.
For the same natural rubber samples the $^1$H dipolar encoded LM decays were recorded on a solid-state Bruker DSX 500 NMR spectrometer using the same pulse sequence (cf. Fig. 4.3b) with a pulse flip angle of about $\theta = 60^0$. The signal decays are shown in Fig. 4.8 together with the initial $\tau^2$ dependence (inset). From eq. [4.16] one gets the ratio of the square of the $^1$H residual dipolar couplings for the natural rubber samples NR1 and NR5 as $\frac{\langle \omega_d^2 \rangle_{LM}^{NR1}}{\langle \omega_d^2 \rangle_{LM}^{NR5}} \cong 3.3$ from the data presented in the inset of the Fig. 4.8, and $\frac{\langle \omega_d^2 \rangle_{LM}^{NR5}}{\langle \omega_d^2 \rangle_{LM}^{NR1}} \cong 3.1$ from the data shown in Fig. 4.7 (NMR-MOUSE®). Within the limit of the experimental error these ratios are in good agreement thus showing that the approximations involved in the derivation of eq. [4.16] are justified. Moreover, the residual dipolar couplings measured in homogeneous and inhomogeneous magnetic fields differ by about 10% proving that the NMR-MOUSE® can provide quantitative values for ratios of the total $^1$H residual dipolar couplings for elastomers. We can remark here that in the regime of long excitation times, the dipolar encoded LM decays could be slightly different for the measurements performed with the NMR-MOUSE® and high-field NMR spectrometers as a result of a possible field dependence of the transverse relaxation rate.

### 4.4.1.2 Strained elastomers

Proton dipolar encoded LM decay curves were also measured using the NMR-MOUSE® for the natural rubber band NR1 in the relaxed state (extension ratio $\lambda = 1$) and strained to $\lambda = 2.25$. The extension ratio under an uniaxial force is defined as $\lambda = L/L_0$, where $L$ is the length of the sample under the action of uniaxial force $\vec{F}$ and $L_0$ is the length of the sample for $\vec{F} = 0$. Under mechanical stress the segmental order is increased in elastomers [Call, Sot] and therefore, the residual dipolar couplings will increase because of the more intense interchain excluded-volume interactions [Bre1, Bre2]. This effect is evident in the dipolar encoded LM decay curves presented in Fig. 4.9. From the slopes of the dipolar encoded LM decays shown in the inset of Fig. 4.9 the ratio of the squares of $^1$H residual dipolar couplings can be obtained: $\frac{\langle \omega_d^2 \rangle_{LM}^{\lambda=2.25}}{\langle \omega_d^2 \rangle_{LM}^{\lambda=1}} \cong 1.4$. This value is different from the ratio

---

1 The measurements on the DSX 500 Spectrometer were performed by Dr. Claudiu Filip
\[
\left(\omega_{D}^{\lambda}\right)_{\lambda=2.25}^{\text{LM}} / \left(\omega_{D}^{\lambda}\right)_{\lambda=1}^{\text{LM}} \equiv 1.24
\]
measured by the same techniques on a different natural rubber band using a Bruker DSX-200 spectrometer [Schn3]. This is due to the different values of the cross-link density of the investigated elastomers.

![Graph](image)

**Fig. 4.19:** $^1$H normalized dipolar encoded LM decay curves of a natural rubber sample for two elongation ratios $\lambda=1.00 (\bullet)$ and $\lambda=2.25 (\triangle)$ measured by the NMR-MOUSE®. The decay curves were recorded using the same procedure and parameters as discussed in Fig. 4.7. The inset shows the linear dependence on $\tau^2$ (solid lines) for the decay curves in the initial excitation/reconversion regime.

### 4.4.1.3 Angular dependence

It is well known that the residual dipolar and quadrupolar couplings depend on the angle between the direction of the static magnetic field $B_0$ and the direction of the applied uniaxial force for elastomer materials [Call, Sot]. In the case of the NMR-MOUSE® because of the $B_0$ inhomogeneities an effective orientation angle ($\Theta$) can be defined between the direction of the applied force and the axis oriented perpendicular to the permanent magnet faces (z-direction).

Figure 4.10 makes obvious the dependence of $^1$H normalized dipolar encoded LM decay curves of a stretched ($\lambda=2.5$) natural rubber sample on $\Theta$. The angular dependence of the rate of dipolar encoded LM signals measured with the NMR-MOUSE® for fixed excitation/reconversion times of $\tau=0.5$ ms is shown in Fig. 4.11. The dependence of the normalized signal shows a broad minimum around an angle close to the magic angle of $\Theta_m=54.7^0$. It was also shown that the transverse
relaxation rate $1/T_2$ has a strong anisotropy in oriented tissues [Hak] having a minimum at the magic angle. Figure 4.12 shows the angular dependence of the reciprocal value of the Hahn echo intensity for the same elastomer under identical conditions. It is obvious that the tendency is very similar, due to the dependence on the square of the second Legendre polynomial $P_2(\cos \Theta(\vec{r}))$.

Fig. 4.20 $^1$H normalized dipolar encoded LM decay curves of a stretched ($\lambda = 2.5$) natural rubber sample for three $\Theta$ values ($0^\circ$, $54.7^\circ$ and $90^\circ$) measured by the NMR-MOUSE$^\text{®}$. $\Theta$ represents the angle between the direction of the applied force and the axis oriented perpendicular to the permanent magnet faces (z-direction). The decay curves were recorded using the same procedure and parameters as discussed in Fig. 4.7.
Fig. 4.21 a) Angular dependence of the $^1$H normalized dipolar encoded LM signal for the natural rubber sample NR1 with elongation ratio $\lambda=2.5$ measured by the NMR-MOUSE®. The angle between the direction of the uniaxial stress force and the axis perpendicular to the faces of the permanent magnet is denoted by $\Theta$. The LM signals have been recorded using the pulse sequence of Fig. 4.3b and the phase cycle of Table 4.1 for $\tau = 0.5$ ms. The LM signals were normalized to the intensity of the Hahn echo recorded with the same echo time as that used for LM signals. b) A polar plot from a). The measurements in the range 0-90° were extended for the whole trigonometric circle.

Fig. 4.22 a) Angular dependence of the Hahn echo intensity for the natural rubber sample NR1 with elongation ratio $\lambda=2.5$ measured by the NMR-MOUSE®. The angle between the direction of the uniaxial stress force and the axis perpendicular to the faces of the permanent magnet is denoted by $\Theta$. The intensities of the Hahn echo were recorded with the same echo time as that used for LM measurements (0.1 ms). b) A polar plot from a). The measurements in the range 0-90° were extended for the whole trigonometric circle.
4.4.1.4 Other Applications

The applicability of this method for determining the residual dipolar couplings in elastomers was tested on other elastomers like SBR with different cross-link densities and natural rubber samples with different fillers. One can see in Fig. 4.13 that three differently cross-linked samples (SBR 1-3) are fully distinguishable by measuring the decay of the dipolar encoded LM. The signal of the sample with a higher cross-link density decays faster (SBR 3) than the signal of lower cross-linked SBR 1. The proton residual dipolar couplings increase in proportion with cross-link density and therefore, with increasing amount of the vulcanization system the maximum of the signal intensity is shifted to shorter excitation times.

Fig. 4.23 $^1$H normalized dipolar encoded LM decay curves for the SB rubber samples SBR1 (■) SBR2 (▲) and SBR3 (○) which differ in cross-link density. The decay curves have been recorded with the NMR-MOUSE® using the pulse sequence of Fig. 4.3b and the phase cycle of Table 4.1. The dipolar encoded LM signals were normalized to the intensity of the Hahn echo recorded with the same echo time as that used for the decay curves.

This technique was also applied to characterize reference natural rubber samples with different cross-link density and carbon black and silica fillers. In addition to the chemical cross-link density the carbon black and silica fillers are also expected to modify the polymer chain mobility [Blü]. An increase in the $^1$H residual dipolar couplings is expected for filled elastomers compared to unfilled samples. Nevertheless, this effect is not observed for natural rubber [Kühn]. Within the limits of
experimental error the slope of the LM decay curves are identical and independent of
the filler concentration and the types of fillers.

4.4.2 ¹H double-quantum build-up curves

4.4.2.1 Natural Rubber
The possibility to excite ¹H DQ filtered signals using the NMR-MOUSE® and the
pulse sequence presented in Fig. 4.3b is proved by the DQ build-up curves in Fig.
4.14 recorded on the natural rubber samples NR1 and NR5 (cf. Table 4.4). In the
initial pumping regime the slope of the DQ build-up curves are different reflecting
different values of the residual dipolar couplings. The signal-to-noise ratio is relatively
low making the quantitative evaluation of residual dipolar couplings inaccurate. A
better sensitivity to the cross-link density is given by the times at which DQ build-up
curves reach the maximum values. This is due to the combined effect of the
increasing efficiency of pumping DQ coherences with increasing
excitation/reconversion times in the initial pumping regime and transverse relaxation
of the single-quantum coherences [Gra], [Schn1]. Both quantities are affected by the
cross-link density. For multi-spin dipolar networks higher-order multiple-quantum
coherences and spin correlations will also be excited and contribute to the decrease
of the DQ signal amplitudes.
Fig. 4.24: $^1$H normalized DQ build-up curves for the natural rubber samples NR1 (Δ) and NR5 (•) with different cross-link densities (cf. Table 4.4) using the NMR-MOUSE®. The build-up curves have been recorded using the pulse sequence of Fig. 4.3b. The DQ signals were normalized to the intensity of the Hahn echo recorded with the same echo time as that used for the build-up curves.

Fig. 4.25 The normalized DQ build-up curves recorded with Bruker DSX 500 NMR spectrometer. The pulse sequence of Fig. 4.3b was used with the pulse flip angle of about $\theta =60^\circ$ and the pulse delays identical with that used in the measurements with the NMR-MOUSE®. The inset shows the dependence on $\tau^2$ for the build-up curves in the initial excitation regime. The solid lines represent the best fit of the data with a polynomial function of order six in $\tau$. 
In order to test the efficiency of the phase cycling scheme used for filtering DQ coherences and to partially mimic the distribution of rf pulse flip angles the $^1$H DQ build-up curves of NR1 and NR5 have been recorded on a Bruker DSX 500 solid-state NMR spectrometer using the pulse sequence presented in Fig. 4.3b with $\theta = 60^\circ$ (cf. Fig. 4.15). The data obtained on the DSX 500 and on the NMR-MOUSE® show good agreement. The inset of Fig. 4.15 shows the evolution of the DQ filtered signal intensities in the initial excitation time regime versus $\tau^2$. The lines represent the best fit of the data with a polynomial function of order six in $\tau$. The coefficient of the $\tau^2$ term are related to $\langle \tilde{\alpha}_D^2 \rangle$ [Gra, Schn1]. We can note here that the DQ build-up curves in the regime of long excitation times could be slightly different for the measurements performed with the NMR-MOUSE® and high-field NMR spectrometers as a result of a possible dependence of the transverse relaxation rate on the magnetic field strength. Nevertheless, this effect was not observed for the investigated series of the cross-linked natural rubber. The maximum of the DQ build-up curves recorded at 20.1 MHz and 500 MHz are reached for the same $\tau$ values (cf. Fig. 4.14 and Fig. 4.15).

Strained Elastomers

Proton DQ build-up curves have been recorded with the NMR-MOUSE® sensor for a relaxed (i.e., $\lambda=1$) and stretched ($\lambda=2.25$) natural rubber sample. The data are shown in Fig. 4.16. The low signal-to-noise ratio in the initial regime of the build-up curves leads to errors in the estimation of the residual dipolar couplings. Nevertheless, the DQ build-up curves clearly show a dependence on the $\lambda$ ratio. The maximum of the DQ build-up curves (dashed lines in Fig. 4.16) is shifted to an earlier time for the stretched elastomer. This fact is mainly a combination of two effects: (i) the differences in the $^1$H residual dipolar couplings (i.e., $\langle \tilde{\alpha}_D^2 \rangle^{\text{DQ}}_{\lambda=2.25} > \langle \tilde{\alpha}_D^2 \rangle^{\text{DQ}}_{\lambda=1}$), and (ii) differences in the transverse relaxation rates of the single-quantum coherences (i.e., $T_2 (\lambda=2.25) < T_2 (\lambda=1)$). When we recorded the Hahn echo decays with the NMR-MOUSE® for the two elongation ratios discussed above and fitted the long decay components to an exponential function, different effective transverse relaxation times $T_2 (\lambda=1)=1.79$ ms and $T_2 (\lambda=2.25)=1.12$ ms are obtained.

ii The measurement was performed by Dr. Claudiu Filip
Fig. 4.26 $^1$H normalized DQ build-up curves measured by the NMR-MOUSE® for the natural rubber sample for two elongation ratios $\lambda=1.00$ (●) and $\lambda=2.25$ (△) (left side) and DQ build-up curves for the natural rubber sample NR1 for the elongation ratio $\lambda=2.25$ by the first elongation (△) and after a relaxing time of about 30 Min. and re-elongation to the same length (●) (right side). The build-up curves have been recorded using the pulse sequence of Fig. 4.3b and the phase cycle of Table 4.2. The DQ signals were normalized to the intensity of the Hahn echo recorded with the same echo time as that used for build-up curves. The position of the maximum for each build-up curve is marked by a dashed line.

When we let the sample reposing after the first elongation for a time and re-stretch it to the same elongation ratio as above, the maximum of the DQ build-up curve moves again to a lower value (Fig. 4.16 right). A possible cause of this tendency is that after the first elongation the chain arrangement does not fully disappear. The chains need a time period to return in complete equilibrium and we start to strain the sample from different pre-conditions as by the first elongation (Mullins effect). As a result we see that the residual dipolar couplings and transverse relaxation rates are different. It is fascinating that such a difference is observable with the NMR-MOUSE® in such inhomogeneous magnetic fields. This topic needs further investigations in the future.

### 4.4.2.3 Angular dependence

The dependence of the residual dipolar couplings on the angle between the direction of the static magnetic field $B_0$ and the direction of the applied uniaxial force for an natural rubber sample is investigated. In Fig. 4.17 the dependence of the DQ build-up curves on this angle $\Theta$ is depicted. It is obvious that the maximum of the build-up curves is changing for the representative angles 0°, 90° and magic angles related to...
the second Legendre polynomial in the same way as $1/T_2$: the minimum value appears for $\Theta = 0^\circ$ and the maximum value for $\Theta = 54.7^\circ$.

The angular dependence of the $^1$H DQ filtered signals measured with the NMR-MOUSE® for NR1 band with $\lambda = 2.5$ and excitation/reconversion times of $\tau = 0.5$ ms and $\tau = 1.6$ ms are shown in Fig. 4.18. These times correspond to the rising part and the decaying part of the DQ build-up curve. The angular dependences show a broad minimum and a broad maximum around an angle close to the magic angle of $\Theta_m = 54.7^\circ$. The rising part of the DQ build up curve is dominated by the residual dipolar couplings and is described by a function which contain terms of the form
\[
\left\langle (\langle \Theta \rangle)^{2n} \right\rangle_v \propto \left\langle (P_n(\cos \Theta(\vec{r})))^{2n} \right\rangle_v, \quad (n=1,2,3...) \text{ where } P_n(\cos \Theta(\vec{r})) \text{ is the Legendre polynomial of second order in } \cos \Theta(\vec{r}).
\]
The angle $\Theta(\vec{r})$ is the angle between the local static magnetic field $\vec{B}_0(\vec{r})$ and the force $\vec{F}$. The average over the sensitive volume of the NMR-MOUSE® is denoted by $\langle ... \rangle_v$ and is taking into account the distribution in the orientation of $\vec{B}_0$. It is obvious that the intensity of the DQ filtered signal has a minimum value at the magic angle $\Theta_m$ when in some region of the sensitive volume $\vec{B}_0$ is oriented at this angle relative to $\vec{F}$. Furthermore, the strong inhomogeneities in the orientation of the static magnetic field make the ratios $S_{DQ}(\Theta = 0)/S_{DQ}(\Theta_m)$ and $S_{DQ}(\Theta = 0)/S_{DQ}(\Theta = 90^\circ)$ different from the expected $\Theta$ dependence given by the Legendre polynomial of second order (Fig. 4.18). In the decay region of the DQ build-up curve the intensity of the filtered signal is dominated by the transverse relaxation ($T_2$) of the SQ coherences. It was shown that $1/T_2$ has a strong anisotropy in oriented tissues [Hak] having a minimum for the magic angle. Therefore, the attenuation of the DQ filtered signal is minimized and the signal has a maximum value, as it is evident from Fig. 4.18. In this regime of the excitation/reconversion the anisotropy of the DQ filtered signal is reduced compared to the initial regime because of the opposite contribution to the signal intensity given by the residual dipolar couplings and transverse relaxation.
Fig. 4.27 $^1$H normalized DQ build-up curves measured by the NMR-MOUSE® for the stretched natural rubber sample ($\lambda=2.5$). $\Theta$ represents the angle between the direction of the applied force and the axis oriented perpendicular to the permanent magnet faces (z-direction). The decay curves were recorded using the same procedure and parameters as discussed in Fig. 4.14.

Fig. 4.28: Angular dependence of the $^1$H normalized DQ build-up curves for the natural rubber sample NR1 with elongation ratio $\lambda=2.5$ measured by the NMR-MOUSE®. The angle between the direction of the uniaxial stress force and the axis perpendicular to the faces of the permanent magnet is denoted by $\Theta$. The DQ filtered signals have been recorded using the pulse sequence of Fig. 4.3b and the phase cycle of Table 4.2 for $\tau=0.5$ ms (■) and $\tau=1.6$ ms (○). The DQ signals were normalized to the intensity of the Hahn echo recorded with the same echo time as that used for DQ filtered signals.
4.4.2.4 Dipolar encoded LM and DQ coherences for characterising the spatial distribution of chain orientation in stretched elastomers

The possibility to map the strain distribution in elastomers is demonstrated in this chapter with the NMR-MOUSE® on a natural rubber band stretched to \( \lambda = 2.5 \) in the direction of the main magnetic field, which has a cut at one side (see Fig. 4.20). The subsequently induced inhomogeneous strain distribution is similar to the one used for \(^2\)H and for \(^1\)H mapping by NMR imaging [Klin1, Klin2, Schn3].
The spatial distribution of the chain orientation was recorded by measuring a Hahn echo for a fixed echo time, the value of the dipolar encoded longitudinal magnetization and of the double quantum signal for a fixed excitation/reconversion time (0.5 ms and 1.2 ms respectively). The pulse sequence depicted in Figure 4.3b was used. The investigated parameters show a direct dependence on the square of the second Legendre polynomial of second order $P_2(\cos \Theta)$, where in our case the effective orientation angle ($\Theta$) can be defined between the direction of the applied force and the axis oriented perpendicular to the permanent magnet faces ($z$-direction). The strong inhomogeneities in the orientation of the static magnetic field make the differences $|I_{DQ}(\Theta = 0) - I_{DQ}(\Theta = \theta)|$ and $|I_{DQ}(\Theta = 0) - I_{DQ}(\Theta = 90)|$ different from the expected $\Theta$ dependence given by the Legendre polynomial. Nevertheless we exploited these intervals for the evaluation of the anisotropy contrast of the reading points represented in Figure 4.18. The highest values are expected for the experimental points where the highest changes in the residual dipolar couplings exist as a result of increased segmental order induced by mechanical stress.
Fig. 4.31 The spatial distribution of the chain orientation of strained natural rubber band at $\lambda=2.5$ with a single cut weighted by residual dipolar couplings using the LM, DQ and Hahn echo signal intensities. On the x-axis the reading positions from Fig. 4.20 are represented and position 1 and 2 are the average values of 1 with 1' and 2 and 2' respectively.

The highest strain is located at the centre of the cut (position 3 in Fig. 4.18), which is clearly represented by the highest values for the anisotropy contrast $|I_{0^\circ} - I_{90^\circ}|$ and $|I_{0^\circ} - I_{55^\circ}|$ (Fig. 4.19). The DQ weighted signal shows the highest contrast between these values (in comparison to LM and Hahn echo), due to the high sensibility of this parameter to the residual dipolar couplings. In the two lips of the cut (position 2 and 2’ in Fig. 4.18) the strain is lower than in the middle, but still higher than in position 1 and 1’.

4.4.3 The transverse relaxation of the DQ coherences

The transverse relaxation time of the DQ coherences $T_{2DQ}$ has been measured using the pulse sequence from Fig. 4.3 by keeping the excitation/reconversion times $\tau$ fixed and incrementing the evolution time $\tau_1$. Fig. 4.22 represents the decay of the normalized DQ intensity measured by the NMR-MOUSE© for NR1 in comparison with NR5 with a higher cross-link density.
Fig. 4.32 DQ relaxation curves for the natural rubber samples NR1 (○) and NR5 (▲) (cf. Table 4.4) using the NMR-MOUSE®. The curves have been recorded using the matched pulse sequence of Fig. 4.3, with fixed excitation/reconversion times $\tau$ and variable evolution time $t_1$.

Fig. 4.33 DQ relaxation curves for the natural rubber samples NR1 (○) and NR5 (▲) (cf. Table 4.4) recorded with a Bruker DSX 500 NMR spectrometer. The curves have been recorded using the matched pulse sequence of Fig. 4.3, with fixed excitation/reconversion times $\tau$ and variable evolution time $t_1$.

After a monoexponential evaluation of the curves we get the times $T_{2\text{DQ}}$ (NR1): 1,5 ms, resp. 0,5 ms for NR5. This meets one’s expectations, that the DQ signal of the
higher cross-linked sample decays much faster than that from the lower cross-linked elastomer. If we mimic the same measurement in homogeneous fields employing Bruker DSX 500 NMR spectrometer one can observe a similar behaviour of the curves for the two samples ($T_{2DQ}$ (NR1): 0.3 ms, resp. 0.2 ms for NR5), but a much faster decay in comparison with the measurements in inhomogeneous fields. This effect is related to the differences between the transverse relaxation rates of double-quantum coherences at 500 MHz and 20 MHz.

### 4.4.4 DQ Decay Curves

#### 4.4.4.1 Natural rubber

In order to improve the signal-to-noise ratio for the DQ filtered signals a new procedure was introduced based on the MERE pulse sequence (cf. Fig. 4.4b). The $^1$H normalized DQ decay curves measured using the NMR-MOUSE® and the Bruker DSX 500 spectrometer for the natural rubber samples NR1 and NR5 which differ in cross-link density (cf. Table 4.4) are presented in Figs. 4.24 and 25, respectively. The ratio of the slopes for the fitted straight lines in $\tau^{-2}$ involves the $\langle \omega_D^2 \rangle$ term (see Eq. [4.22]) for the two natural rubber samples NR5 and NR1. This ratio (see below) is in good agreement (within about 10%) with the ratio obtained from the measurements performed with the NMR-MOUSE®.

To justify the approximations used for the derivation of Eq. [4.22] a comparison between the $\langle \omega_D^2 \rangle$ values measured from DQ build-up and decay curves was made. For this purpose the data recorded with the Bruker DSX 500 spectrometer shown in Figs. 4.15 (see inset) and 4.25 were used. For the natural rubber samples NR1 and NR5 we get the ratios $\langle \omega_D^2 \rangle_{NR5}^{DQ \text{ buildup}} / \langle \omega_D^2 \rangle_{NR1}^{DQ \text{ buildup}} \equiv 2.5$ from the data presented in the inset of the Fig. 4.15, and $\langle \omega_D^2 \rangle_{NR5}^{DQ \text{ decay}} / \langle \omega_D^2 \rangle_{NR1}^{DQ \text{ decay}} \equiv 3$ from the data shown in Fig. 4.25. Within the limit of experimental errors these ratios are in good agreement thus showing that the approximations involved in the derivation of Eq. [4.22] are reasonable.
Fig. 4.34: $^1$H normalized DQ decay curves for the natural rubber samples NR1 (Δ) and NR5 (●) (cf. Table 4.4). The DQ decay curves have been recorded using the MERE pulse sequence of Fig. 4.4b. The DQ filtered signal recorded using the NMR-MOUSE® versus $\tau^2$, where $\tau'$ is the mismatched reconversion time.

Fig. 4.35: The normalized DQ decay curves recorded with Bruker DSX 500 NMR spectrometer versus $\tau^2$. The pulse sequence of Fig. 4.4b was used with the pulse flip angle of about $\theta = 60^0$ and pulse delays identical to those used in the measurements with the NMR-MOUSE®. The DQ signals were normalized to the maximum intensity of the DQ build-up curves. The solid lines represent the best fit of the experimental data in the initial $\tau^2$ regime of mismatched reconversion.
In order to investigate the possibility to use the NMR-MOUSE\textsuperscript{®} sensor to measure the ratio of the total (intra- as well as inter-group) residual dipolar couplings of two samples, with one sample used as a reference, \(^1\)H DQ decay curves have been recorded for the natural rubber cross-link series of Table 4.4. The initial decay time regime \(\tau'\) was exploited to evaluate the values of the square of the total residual dipolar coupling given by \(\langle \omega^2 \rangle\) (cf. Eq. [4.22]). The measurements were performed on a NMR-MOUSE\textsuperscript{®} and a Bruker DSX 500 spectrometer using the \(\tau\) values (cf. Fig. 4.4b) corresponding to the maximum of DQ build-up curves for each sample in the cross-linked series. The residual dipolar coupling ratios \(\frac{\langle \omega^2_{d,NR1} \rangle^{1/2}}{\langle \omega^2_{d,NR2} \rangle^{1/2}}\), for different natural rubber samples labelled by indices i=1, 2, 3, 4 and 5 (see Table 4.4) are shown in Fig. 4.26 versus sulphur-accelerator content in phr. In the limit of experimental errors these ratios show a linear dependence. This linear dependence underlines again the validity of the simple model employed for evaluating residual dipolar couplings [Sot2] which has been used previously in studies of polybutadiene [Gra, Dem1, Gas] and synthetic 1,4-cis-polyisoprene [Schn1]. However, the lines in Fig. 4.26 do not cross the origin but provide a finite value for residual dipolar couplings for uncross-linked natural rubber. As noted before [Sot2] this is not in contradiction with the applied model, but reflects the influence of the local chain order (physical cross-links). It is evident from Fig. 4.26 that over the range of cross-link densities that have been examined, there is an about 80% increase in the normalized value of the residual dipolar couplings. The residual dipolar couplings measured in homogeneous and inhomogeneous magnetic fields differ by about 10% proving that the NMR-MOUSE\textsuperscript{®} can provide quantitative values for relative \(^1\)H total residual dipolar couplings of elastomers.
Fig. 4.36 The normalized values of the residual dipolar couplings \( \left\langle \frac{\omega_{d,NRI}}{\omega_{d,NRI}} \right\rangle^{1/2} / \left\langle \frac{\omega_{d,NRI}^2}{\omega_{d,NRI}^2} \right\rangle^{1/2} \), for the cross-linked natural rubber series of Table 4.4 versus sulphur-accelerator content. These quantities are determined by measuring the slopes of the DQ decay curves represented versus \( \tau^2 \), (cf. Fig. 4.24). The ratios \( \left\langle \frac{\omega_{d,NRI}^2}{\omega_{d,NRI}^2} \right\rangle^{1/2} / \left\langle \frac{\omega_{d,NRI}^2}{\omega_{d,NRI}^2} \right\rangle^{1/2} \) for \( i = 2, 3, 4 \) and 5, are obtained from the data recorded using the NMR-MOUSE® (circles) and the Bruker DSX 500 spectrometer (triangles) employing the MERE pulse sequence (cf. Fig. 4.4b). The continuous and dashed lines represent the best fits of the \( \left\langle \frac{\omega_{d,NRI}^2}{\omega_{d,NRI}^2} \right\rangle^{1/2} / \left\langle \frac{\omega_{d,NRI}^2}{\omega_{d,NRI}^2} \right\rangle^{1/2} \) ratios measured with the NMR-MOUSE® and the DSX 500 spectrometer.

4.4.4.2 Strained Elastomers
Proton DQ decay curves have been recorded with the NMR-MOUSE® sensor for a relaxed (i.e., \( \lambda = 1 \)) and stretched (\( \lambda = 2.25 \)) natural rubber sample. The data are shown in Fig. 4.27. A better signal-to-noise ratio than in the initial regime of the build-up curves can be obtained using filtered DQ decay curves recorded with the MERE method (Fig. 4.4). From the linear \( \tau^2 \) dependence it is possible to evaluate the ratio of the square of the residual dipolar couplings (see above). We obtain the value \( \left\langle \frac{\omega_{D,\lambda=2.25}^{2,\text{DQ}}}{\omega_{D,\lambda=1}^{2,\text{DQ}}} \right\rangle \cong 0.73 \) which is in a good agreement with the value of 0.7 measured from dipolar encoded LM decays (see above).
Fig. 4.37 $^1$H normalized DQ decay curves of the natural rubber sample NR1 for two elongation ratios $\lambda = 1.00$ (•) and $\lambda = 2.25$ (△) measured by the NMR-MOUSE® in the initial excitation/reconversion time regime. The decay curves have been recorded using the MERE pulse sequence (Fig. 4.4). The DQ signals were normalized to the intensity of the Hahn echo recorded with the same echo time as that used for the decay curves. The solid lines show the linear dependence on $\tau^2$ for the decay curves in the initial excitation/reconversion regime.

4.4.5 Dipolar order

4.4.5.1 Natural rubber

Build-up curves of proton dipolar order originating from the residual dipolar couplings can be measured in elastomers using the NMR-MOUSE® i.e., in the presence of strongly inhomogeneous magnetic fields. Figures 4.28 and 4.29 show the DO build-up curves recorded with the pulse sequence of Fig. 4.5b for the NR1 and NR5 samples by the NMR-MOUSE® sensor and the Bruker DSX 500 spectrometer, respectively. As expected, the rising initial slope of the DO build-up curve for the natural rubber NR5 with the higher value of the cross-link density is larger than that of the sample NR1. The position of the maximum of the curves (dashed lines) are shifted as expected from the differences in residual dipolar couplings and transverse relaxation rates. Nevertheless, the maximum of the DO build-up curves measured with the Bruker DSX 500 spectrometer are both shifted to lower values compared to those measured with NMR-MOUSE®. This effect is related to the differences between
the transverse relaxation rates of single-quantum coherences at 500 MHz and 20 MHz.

Fig. 4.38 $^1$H normalized DO build-up curves for the natural rubber samples with different cross-link densities measured by the NMR-MOUSE®. The build-up curves have been recorded using the pulse sequence of Fig. 4.5 and the phase cycle of Table 4.3. The DO signals were normalized to the intensity of the Hahn echo recorded with the same echo time as that used for the DQ build-up curves.

Fig. 4.39 $^1$H normalized DO build-up curves for the natural rubber samples with different cross-link densities measured with the Bruker DSX 500 NMR spectrometer. The build-up curves have been recorded using the pulse sequence of Fig. 4.5 and the phase cycle of Table 4.3.
From Figs. 28 and 29 it is evident that the efficiency of detecting signals filtered according to DO in inhomogeneous low magnetic fields is almost an order of magnitude lower compared to that of experiments performed in homogeneous fields. Therefore, no effort was done to extract the ratio of the $^1$H residual dipolar couplings from the experiments performed with the NMR-MOUSE®.

### 4.4.5.2 Strained Elastomers

The DO build-up curves are also sensitive to the strain of elastomers. This effect is shown for the sample NR1 for the two elongation ratios $\lambda=1$ and $\lambda=2.25$ (cf. Fig. 4.30). The maximum of both DO build-up curves are shifted to shorter times compared to the corresponding DQ build-up curve. This effect is due to the differences in the encoding efficiency of $^1$H residual dipolar couplings. This efficiency of dipolar encoding is higher for the DO build-up curves compared to that for the DQ build-up curves as can be seen from the different multiplication factors of the $\langle (\tilde{\omega}_D)^2 \rangle \tau^2$ terms in Eqs. [4.17], and [4.28], respectively.

![Fig. 4.40](image)

**Fig. 4.40** $^1$H normalized DO build-up curves for the natural rubber sample NR1 for two elongation ratios $\lambda=1.00$ (•) and $\lambda=2.25$ (△) measured by the NMR-MOUSE®. The build-up curves have been recorded using the pulse sequence of Fig. 4.5 and the phase cycle of Table 4.3. The DO signals were normalized to the intensity of the Hahn echo recorded with the same echo time as that used for build-up curves. The positions of the maximum for each build-up curve are marked by dashed lines.
4.4.6 Dipolar relaxation time

The most obvious application of the Jeener echo is to measure $T_{1D}$ by plotting echo amplitude vs. time spent in a state of dipolar order. This is measured in elastomers using the NMR-MOUSE® i.e., in the presence of strongly inhomogeneous magnetic fields. Figure 4.31 illustrates the DO signal decays recorded with the pulse sequence of Fig 4.5b for the NR1 and NR5 samples by the NMR-MOUSE® sensor, by keeping the excitation/reconversion times $\tau$ fixed and incrementing the evolution time $t_1$. As expected, the decay of the DO signal for the natural rubber NR5 with the higher value of the cross-link density is faster than that of the sample NR1, because of the differences in residual dipolar couplings and transverse relaxation rates. In comparison the other parameters studied in this work for cross-link series of elastomers, there are only small differences in the case of the dipolar relaxation time.

![Graph showing DO relaxation curves for NR1 and NR5](image)

**Fig. 4.4.41** DO relaxation curves for the natural rubber samples NR1 (○) and NR5 (▲) (cf. Table 4.4) using the NMR-MOUSE®. The curves have been recorded using the pulse sequence of Fig. 4.4.5, with fixed excitation/reconversion times $\tau$ and variable evolution time $t_1$. 
4.5. Conclusions

The possibility to excite and detect various multipolar spin states like dipolar encoded longitudinal magnetization, double-quantum coherences and dipolar order in strongly inhomogeneous magnetic fields was proved by experiments with the NMR-MOUSE®. To partially mimic the effects of the field inhomogeneities on the excitation/reconversion evolution of various multipolar spin states the methods employed were tested on a solid-state Bruker DSX 500 NMR spectrometer using the same pulse sequences as for the NMR-MOUSE® with an arbitrary value of the pulse flip angle. As was shown by the evaluation of the spin system response for an ensemble of dipolar coupled spin-pairs $\frac{1}{2}$ the distribution of pulse flip angles in the inhomogeneous magnetic fields leads to the simultaneous excitation of many spin states. The success of filtering individual multipolar spin states in inhomogeneous fields is related mainly to the fact that even in inhomogeneous fields the phases of the radio-frequency pulses are the same for all the voxels in the sample.

The newly introduced method of DQ decay curves is characterized by an improved accuracy in measuring the ratio of the residual dipolar couplings as a result of better signal-to-noise ratio as compared to the DQ buildup curves. Nevertheless, for optimum setting of this method, the DQ buildup curve has to be recorded first. Moreover, DQ decay curves are less sensitive to the changes in the value of the residual dipolar couplings as compared to the DQ buildup curves. It was also shown that samples having different values of the total residual dipolar couplings in a cross-linked elastomer series can be compared quantitatively using the NMR-MOUSE. The method of the DQ decay curves can be also applied in the case of experiments done in homogeneous magnetic fields or under magic-angle sample spinning for measuring chemically site selective dynamic order parameters. Moreover, this procedure can be used for $^1$H NMR contrast filters to record parameter images of residual dipolar couplings in elastomers having better spatial resolution than images with filters based on DQ buildup coherences.

Compared to MQ coherences, the LM spin state is characterized by a larger NMR signal, which is an important feature especially for low-frequency NMR sensors like the NMR-MOUSE®. In principle, the LM spin state is excited simultaneously for spins in isotropic and anisotropic/restricted environments. Nevertheless, the decay of dipolar encoded LM with increasing the excitation/reconversion times is related to the solid-like behavior of heterogeneous soft solids.
The possibility to detect signals filtered according to $^1$H dipolar order which originate only from the spins in the solid-like environments expands the sphere of applications of the NMR-MOUSE® for measuring macroscopic properties of elastomers and other soft solid matter affected by the segmental dynamics. The Jeener-Broekaert scheme [Jeen] is not the only method, which can be employed to produce DO. Also adiabatic demagnetization in the rotating frame could be used with the NMR-MOUSE®. The efficiency of this technique is expected to be higher than that of the Jeener-Broekaert method.

The sensitivity of the dipolar encoded LM, DQ coherences and DO to differences in cross-link density and strain was shown for samples of natural rubber. This extends the panoply of NMR parameters that can be used with the NMR-MOUSE® for establishing structure-property relations of elastomer materials. Moreover, the DQ filtered signals were shown to be sensitive to the angle between the direction of the applied uniaxial force and the direction of the axis along the permanent magnet poles. The results of this work underline the benefits of the NMR-MOUSE® for the analysis of stress-strain effects in elastomers. The use of residual dipolar couplings of protons as a physical quantity sensitive to the segmental orientation in the presence of inhomogeneous strain distributions in elastomers will significantly enhance the sphere of applications of the NMR-MOUSE®. The possibility to record proton dipolar encoded LM and DQ filtered NMR signals suggests the use of the NMR-MOUSE® for characterization of tissue order in connective tissues, muscles and blood vessels [Hak].
5 New method for measuring segmental order in elastomers by the accordion magic sandwich

5.1 The magic and the mixed echo

Another type of echo successfully used particularly in NMR imaging experiments is the magic echo [Schn4, Rhim, Dem2]. Its feature is the efficiency of refocusing the homonuclear dipole-dipole interactions also in multi-center coupled spin systems, even after a time as long as $T_2$ [Blü]. The solid echo does this only for isolated spin pairs (see chapter 3.3.1). After a 90° pulse with a phase direction chosen along the $x$ axis of the rotating frame, time reversal is achieved by the magic sandwich, which consists of two spin lock pulses of duration of $4\tau$ (called burst pulses), enclosed by two 90°, and 90°-y pulses (Fig. 5.1). If the phase of the last sandwich pulse is chosen to be $-y$, a magic echo is generated, whereas for the mixed echo the phase of the respective pulse is opposite [Kimm]. The mixed echo refocuses coherence loss from homo- and heteronuclear dipolar couplings as well as from linear spin interactions (see Table 5.1) like resonance offset, magnetic susceptibility and chemical shift [Mat]. The magic sandwich is followed by another free evolution interval of length $\tau$ after which the magic echo appears. The echo maximum representing the completely refocused coherences is reached after a cycle time of duration $6\tau$. The phase reversal of the burst pulses serves for the compensation of rotating frame phase shifts caused by $B_1$ inhomogeneities (under a rotary echo occurring at $3\tau$).
Fig. 5.42 Magic (-y) and mixed (+y) echo pulse sequence. The 90° flip angle corresponds to a flip angle $\theta$ for the NMR-MOUSE® because of the flip angle distribution.

The magic-echo pulse sequence selectively recovers spin coherences, which have been defocused by multi-center homonuclear spin interactions, i.e. dipolar couplings or quadrupolar couplings. Phase shifts caused by linear spin interactions and by heteronuclear spin couplings are not compensated. With Hahn two pulse echoes the situation is reversed. This pulse sequence refocuses only dephasings caused by linear spin interactions and by bilinear heteronuclear spin couplings (see Tab. 1).

Magic echoes which are formed under dipolar or quadrupolar interactions selectively render signals of the rigid part of the objects, mixed echoes are sensible to rigid as well as soft materials [Blü].

Table 5.7 Comparison of the different echo types used in this chapter from the point of view of their refocusing the dephasing from different spin interactions. The detailed pulse sequences are depicted in Figs. 3.2 and 5.1. To the linear spin interaction belong the chemical shift and magnetic field inhomogeneities.

<table>
<thead>
<tr>
<th></th>
<th>Hahn Echo 90$_x$-180$_y$</th>
<th>Solid Echo 90$_x$-90$_y$</th>
<th>Magic Echo 90$_x$-90$_y$-a$_x$-a$x$-90$_y$</th>
<th>Mixed Echo 90$_x$-90$_y$-a$_x$-90$_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refocused spin interactions</td>
<td>linear</td>
<td>two-spin homonuclear</td>
<td>multi-center homonuclear</td>
<td>multi-center homonuclear</td>
</tr>
<tr>
<td></td>
<td>multi-center heteronuclear</td>
<td>partly multi-center homonuclear</td>
<td>linear</td>
<td>multi-center heteronuclear</td>
</tr>
<tr>
<td>Not refocused spin interactions</td>
<td>multi-center homonuclear</td>
<td></td>
<td>linear</td>
<td></td>
</tr>
</tbody>
</table>
To validate the features of the different echo species, we measured the decays of the different echoes as presented in Table 1 on a cross-linked natural rubber sample (NR5) with the NMR-MOUSE® at 20.1 MHz. In Figure 5.2 the decay curves of the amplitude of the echoes are depicted, obtained by incrementing the echo time $2\tau$ for Hahn and solid echoes and $6\tau$ for magic and mixed echoes. The corresponding time constants, which were obtained by a monoexponential fit of the curves are also depicted in Fig 5.2. According to our expectation the fastest decay is the Hahn decay ($T_2 = 0.4$ ms) because the homonuclear dipolar couplings are not refocused and add to the loss of signal intensity. The solid echo decays with a rate constant between the Hahn and magic echo, because of bilinear dipolar couplings are recovered but with the multi-center couplings. The mixed echo shows the slowest decay, as expected.

![Graph](image)

**Fig 5.43** Comparison of the Hahn, solid, magic and mixed echo decays measured by the NMR-MOUSE® at a Larmor frequency of 20.1 MHz on a cross-linked natural rubber sample (NR5). The echo time is $2\tau$ for Hahn and solid and $6\tau$ for magic and mixed echoes.
5.2 The accordion magic sandwich [Wies3]

5.2.1 Theory

In the following we shall consider a multi-spin system with magnetically equivalent nuclei having spin \( l = 1/2 \) interacting by dipolar couplings. This can be represented by a rigid system or soft solids, in particular elastomers, in which anisotropic molecular motions, fast on the NMR time scales, will lead to residual dipolar couplings [Sot2]. For both cases the secular dipolar Hamiltonian will be denoted by \( H_d^{(0)} \). The magic echo can refocus the spin system evolution for a multi-spin dipolar network under this homogeneous spin interaction [Kimm]. The refocusing of the excited single-quantum coherences by a rf pulse (represented by a \( 90^\circ_y \) pulse (cf. Fig. 5.1)) is performed by a composite pulse called magic sandwich (MS), i.e., \( 90^\circ_y \)-burst pulse_x-burst pulse_x - \( 90^\circ_y \). A high refocusing efficiency of the MS is given by the condition: \( \omega_{ib} >> \omega_d \) where \( \omega_{ib} \) is the angular frequency of the burst pulses and \( \omega_d \) is the angular frequency corresponding to the dipolar local field. This is easily fulfilled, especially for soft solids. These materials are highly heterogeneous from the point of view of molecular motions. Therefore, inhomogeneous echoes can be generated. If at the end of the MS a \( 180^\circ_y \) pulse is added, the transverse magnetization dephasing produced by homogeneous as well as inhomogeneous interactions can be refocused under a mixed echo [Mat]. For a dipolar solid in homogeneous magnetic fields the maximum amplitude of the mixed echo is obtained for the pulse sequence: \( 90^\circ_x - \tau - 90^\circ_y \)-burst pulse_x(2\( \tau \))-burst pulse_x(2\( \tau \))-\( 90^\circ_y - \tau - \text{Mixed Echo} \), presented in Fig 5.1. The amplitude of the mixed echo is not encoded by dipolar or inhomogeneous spin interactions, like external magnetic field inhomogeneities, magnetic sample susceptibility effects, heteronuclear couplings, etc. (see Table 5.1). Nevertheless, the echo amplitude is affected by the relaxation in the laboratory and rotating reference frames.

One possibility to encode the amplitude of the magic echo by the homonuclear dipolar interactions is to use a mismatched MS, i.e., \( 90^\circ_x -(\tau + n\Delta) - 90^\circ_y \)-burst pulse_x(2\( \tau \)-n\( \Delta \))-burst pulse_x(2\( \tau \)-n\( \Delta \))-\( 90^\circ_y -(\tau + n\Delta) - \text{Echo} \) where \( n \) is a
positive or negative integer number \((n \in \mathbb{Z})\) and \(\Delta\) is the decrement or increment time, respectively. We shall call this mismatched MS composite pulse with variable \(n\) as accordion magic sandwich (hereafter AIMS). Another possibility to produce dipolar encoding is given by the use of \(\theta\) sandwich rf pulses or off-resonance burst pulses.

**Fig 5.44** The AIMS pulse sequence. \(\theta\) is the 90° flip angle for the NMR-MOUSE\(^\circledR\) because of the flip angle distribution [Wies3].

In order to evaluate the spin system response to the AIMS sequence we have to define the propagators active during the time intervals (1)-(4) depicted in Fig. 5.3. We can write

\[
\begin{align*}
E_1 &= \exp\{-iH_R(\tau + n\Delta)\}, \\
E_2 &= \exp\{-i[-\omega_{1b}I_x + H_{R}](2\tau - n\Delta)\}, \\
E_3 &= \exp\{-i[+\omega_{1b}I_x + H_{R}](2\tau - n\Delta)\}, \\
E_4 &= \exp\{-iH_R(\tau + n\Delta)\},
\end{align*}
\]

where the total Hamiltonian in the on-resonance rotating reference frame is \(H_R\), and \(\vec{I}(I_x, I_y, I_z)\) is the spin operator vector. The total Hamiltonian is given by

\[
H_R = H_d^{(0)} + H_{\text{inh}},
\]

where \(H_d^{(0)}\) is the secular multi-spin dipolar Hamiltonian and \(H_{\text{inh}}\) is the Hamiltonian describing the inhomogeneous spin interactions, i.e., interactions linear in spin operator \(I_z\).

The propagator describing the MS can be written from eq. [5.1] and has the form

\[
B = P_y \exp\{-i[-\omega_{1b}I_x + H_{R}](2\tau - n\Delta)\}P_y \exp\{-i[+\omega_{1b}I_x + H_{R}](2\tau - n\Delta)\}P_y \left(P_y\right)^2
= \exp\{-i[-\omega_{1b}I_x + P_yH_{R}P_y](2\tau - n\Delta)\}\exp\{-i[+\omega_{1b}I_x + P_yH_{R}P_y](2\tau - n\Delta)\}\left(P_y\right)^2,
\]

\[5.3\]
where the $90^\circ_y$ and $90^\circ_\tau$ pulses have the propagators $P_y = \exp\left\{i\frac{\tau}{2} I_y\right\}$ and $P_\tau = \exp\left\{-i\frac{\tau}{2} I_\tau\right\}$, respectively. The Liouville operator is defined by $\hat{\mathbf{O}}\rho = \mathbf{O}\rho\mathbf{O}^{-1}$, with $\mathbf{O}\mathbf{O}^{-1} = 1$. If the strength of the burst pulses is fulfilling the conditions: $\omega_{\text{i.b}} \gg \omega_d$, and $\omega_{\text{i.b}} \gg \|\mathbf{H}_{\text{inh}}\|$, where $\|\mathbf{H}_{\text{inh}}\|$ is the norm of the Hamiltonian $\mathbf{H}_{\text{inh}}$ this Hamiltonian can be neglected in the spin evolution during burst pulses as well as nonsecular dipolar Hamiltonian. From eq. [5.3] the burst propagator can be written as

$$B = \exp\left\{-i\left[\omega_{\text{i.b}} I_z - \frac{1}{2} \mathbf{H}_d^{(0)}\right](2\tau - n\Delta)\right\}\exp\left\{-i\left[\omega_{\text{i.b}} I_z - \frac{1}{2} \mathbf{H}_d^{(0)}\right](2\tau - n\Delta)\right\}\left(P_y\right)^2,$$  \[5.4\]

and finally has the form

$$B = \exp\left\{\mathbf{H}_d^{(0)}(2\tau - n\Delta)\right\}(P_y)^2.$$  \[5.5\]

Using the above equations the total propagator corresponding to the AIMS pulse sequence (cf. Fig. 5.3) can be obtained and the evolution of the spin system density operator $\rho(t)$ at the time $t=6\tau$ (corresponding to the matched magic echo for $n=0$) is given by

$$\rho(6\tau) = \hat{\mathbf{E}}_4 \hat{\mathbf{E}}_5 \hat{P}_y \rho(0),$$  \[5.6\]

Initially, the spin system is in the thermodynamical equilibrium in the static magnetic field therefore, $\rho(0) \propto I_z$. Using eqs. [5.1] and [5.5] we can get for eq. [5.6]

$$\rho(6\tau) = \exp\left\{-i\hat{\mathbf{H}}_d^{(0)} + \mathbf{H}_{\text{inh}}\right\}(\tau + n\Delta)\exp\left\{-i\hat{\mathbf{H}}_d^{(0)}(2\tau - n\Delta)\right\}$$

$$\times \left[P_y^2\exp\left\{-i\left[\hat{\mathbf{H}}_d^{(0)} + \mathbf{H}_{\text{inh}}\right](\tau + n\Delta)\right\}\right]P_y^2 \rho(0).$$  \[5.7\]

It is evident from the above equation that in the limit of intense burst pulses the refocusing pulse “glue” at the end of the MS is refocusing inhomogeneous spin interactions at $t=6\tau$ producing a Hahn (or inhomogeneous) echo as long as the periods of free evolution are of the same duration. Therefore, the amplitude of the NMR signal at $t=6\tau$ is not encoded by inhomogeneous spin interactions.

The signal obtained by the AIMS pulse sequence which is dipolar encoded and normalized to the mixed echo signal for $n=0$, has the form

$$S(3n\Delta) = \frac{\text{Tr}\left\{I_y \exp\left\{-i\hat{\mathbf{H}}_d^{(0)}(3n\Delta)\right\}I_y\right\}}{\text{Tr}\left\{I_y^2\right\}}.$$  \[5.8\]
Eq. [5.8] shows that the amplitude of the Hahn echo measured at a moment of time \( t=6\tau \) is encoded by the homonuclear dipolar couplings and the time parameter corresponding to this encoding is given by \( 3n\Delta \). The above equation describes the case of AIMS with \( n>0 \), i.e. for compressed MS (as shown in Fig. 5.3) or for \( n<0 \), corresponding to stretched MS. The dipolar encoding is not symmetric around the value \( n=0 \) (*vide infra*). It is evident from eq. [5.7] that a magic echo with the amplitude not affected by the dipolar interactions is present at a moment of time \( t=6\tau+2n\Delta \). As the experimental parameter \( n \) is changing from positive to negative values the magic echo is moving around the Hahn echo occurring at \( t=6\tau \). Actually, the AIMS pulse sequence produces a time disentanglement of the mixed echo present at \( t=6\tau \). The dipolar encoding occurs because the Hahn echo is sampling the magic echo shape.

We neglected so far the effect of transverse relaxation during the coherence evolution in the laboratory and the rotating reference frames. In the presence of this effect the normalized signal described by eq. [5.8] is given by

\[
\frac{S(3n\Delta)}{S(0)} = \frac{\text{Tr}\left\{I_y \exp\left\{-i\mathbf{H}^{(0)}_d(3n\Delta)\right\}I_y\right\}}{\text{Tr}\left\{I_y^2\right\}} \exp\left\{-2n\Delta \left(\frac{1}{T_2} - \frac{1}{T_{2p}}\right)\right\},
\]

where \( T_2 \) and \( T_{2p} \) are the transverse relaxation times in the laboratory and rotating frames, respectively. It is easy to see from eq. [5.9] that a combination of signals taken with AIMS with \( +|n| \) and \( -|n| \) given by

\[
\frac{S(3|n|\Delta)S(-3|n|\Delta)}{S(0)^2} = G(3n\Delta)^2, \tag{5.10}
\]

is not encoded by the transverse relaxations. The function \( G(t) \) describes the magic echo shape affected only by dipolar couplings and is given by

\[
G(t) = \frac{\text{Tr}\left\{I_y \exp\left\{-i\mathbf{H}^{(0)}_d(t)\right\}I_y\right\}}{\text{Tr}\left\{I_y^2\right\}}. \tag{5.11}
\]

Of course, this function describes the free induction decay of the solid-like part of an elastomer [Kimm] and can be represented as an expansion in the van Vleck moments [Kimm]. In the short time limit, i.e. for \( 3n\Delta\omega_d \ll 1 \) we get from eq. [5.10] and eq. [5.11],

\[
\frac{S(3|n|\Delta)S(-3|n|\Delta)}{S(0)^2} \approx 1 - M_2(3n\Delta)^2 + \frac{1}{12}M_4(3n\Delta)^4 - \ldots, \tag{5.12}
\]
where $M_2$ and $M_4$ are the second and forth van Vleck moments, respectively [Kimm]. In the presence of anisotropic molecular motions like in the polymer networks the residual van Vleck moments (hereafter $\overline{M}_{2n}$) can be measured using the procedure defined by eq. [5.12].

The raw data used for generating the combined NMR signal described by eq. [5.12] are given by the normalized amplitude of the Hahn echo taken at $t=6\tau$ which samples the shape of the magic echo (see eq. [5.9]). The signal described by eq. [5.9] can be written in a good approximation for $3n\Delta\omega_d << 1$,

$$\frac{S(3n\Delta)}{S(0)} \approx \left(1 - \frac{1}{2} \frac{M_2(3n\Delta)^2}{4} \frac{M_4(3n\Delta)^4}{16} \cdots \right) \exp \left(-2n\Delta \left(\frac{1}{T_2} - \frac{1}{T_p}\right)\right), \quad [5.13]$$

We can evaluate the dependence of this normalized signal on the mismatch parameter $n\Delta$ (defined in Fig. 5.3) for an elastomer (see below).

### 5.2.2 Experimental

A cross-linked elastomer sample based on commercially available natural rubber (NR5) SMR10 (Malaysia) was investigated. The additives were 3 phr (parts-per-hundred-rubber) ZnO and 2 phr stearic acid. The sulfur and accelerator contents are 5-5 phr. For the sample preparation see chapter 4.3.1.

The $^1\text{H}$ measurements were done at 20.1 MHz, the recycling delay was 0.5 s, pulse length 2.5 $\mu$s (10 dB attenuation) and 400 scans. The echo time is $2\tau$ for Hahn and solid and $6\tau$ for magic and mixed echo. By the AIMS measurements a time period of 50 $\mu$s ($n\Delta$) was sampled with an increment factor of 2 $\mu$s ($\Delta$).

### 5.2.3 Results

To prove the main features of the accordion magic sandwich pulse sequence, the $^1\text{H}$ signal in a cross-linked elastomer sample NR5 (chapter 4.3.1) was detected by the NMR-MOUSE®. The results are depicted in Figure 5.4. For $n\Delta = 0$ the condition of a perfectly timed mixed echo is fulfilled, only one echo is detected. The mixed echo present at the moment of time $6\tau$ consists of a superposition of a magic and a Hahn echo. If a change in the duration of the magic sandwich is allowed (positive and negative $n$ correspond to expanding and compressing the magic sandwich, respectively), two features are evident in the spin system response:
• The amplitude of the mixed echo varies (cf. Fig. 5.5).
• Two echoes are evident for negative values of \( n \) (cf. Fig. 5.4). We have to point out that this effect is not symmetric, as it is shown in Fig. 5.5. This asymmetry is due to the enhanced effect of transverse relaxation for positive values of \( n \) (cf. eq. [5.13]). This is directly related to the fact, that the time period where the Hahn echo maximum appears, does not change, while the maximum of the magic echo is shifted in time.

![Graph](image.png)

**Fig. 5.45** The acquisition time window of the mixed echoes for different accordion times \( n \Delta \). The echo amplitudes vary by compressing the duration of the magic sandwich. The receiver window was open around the value of the echo time \( 6 \tau \) taken as origin in the picture.

The normalized signal intensity at the echo time \( 6 \tau \) is presented in Fig. 5.5 versus \( 3n \Delta \), the accordion time. From eq. [5.13] it is evident, that the variation of the mixed echo amplitude around the value \( 3n \Delta = 0 \) is in good approximation linear in \( 3n \Delta \). This is valid only in the regime \( n \Delta = \ll T_2 \) and \( n \Delta = \ll T_{2\rho} \). For higher values of \( 3n \Delta \) a polynomial dependence is expected. This is comprehensible from Figure 5.5 for \( 3n \Delta \) higher than about 100 \( \mu s \).

Using the data of Figure 5.5 the pure residual dipolar coupling encoded AIMS signal (cf. eq. [5.12]) is presented in Fig. 5.6. The combined data are obtained by multiplication of the normalized intensities of the signal corresponding to the expanding and compressing values of the magic sandwich at the same time interval
$3n\Delta$. The signal is not encoded by the transverse relaxation and exhibits a linear decay with $(3n\Delta)^2$. No attempt was made at this stage (before we can compare the data obtained in homogenous magnetic fields) to extract a value for the residual van Vleck moment.

**Fig. 5.46** The normalized signal intensity versus accordion time $3n\Delta$. A linear dependence around the mixed echo detected for the magic sandwich length of $4\tau$ ($3n\Delta = 0$) is accentuated by a straight line.

**Fig. 5.47** The pure residual dipolar coupling encoded AIMS signal. The multiplication of the normalized intensities of the signal corresponding to the expanding and compressing values of the magic sandwich with the same rate $3n\Delta$ is displayed.
5.2.4 Conclusions

A new NMR method for the investigation of segmental order in soft solids including elastomers via residual van Vleck moments is introduced [Wies3]. It is based on the accordion mixed echo. The main features of this method are related to the fact, that the multi-spin character of the proton dipolar network present in elastomers is taken into account. The theory explaining the attributes of the method was developed for homogeneous fields to predict the properties of the detected signal. Because of the difficulties related to the distribution of the flip angles encountered in the presence of strongly inhomogeneous magnetic fields, this preliminary work has to be confirmed by measurements in homogeneous magnetic fields. These qualitative predictions of the theory are nevertheless in good agreement [cf. Fig. 5.6] with the data obtained on a cross-linked elastomer with the NMR-MOUSE®. 

\[1\] developed by Prof. Dr. D. Demco
6 Integral dispersion of rotating frame spin-lattice relaxation time

6.1 Spin locking

Spin locking is a technique for inhibiting the signal decay in the transversal plane, caused by the field inhomogeneities and local fields. Consider as simple pulse NMR experiment described in terms of the classical formalism. A 90° pulse along the $x'$ axis in the rotating frame generates transverse magnetization along the $y'$ axis. If a second pulse is now applied along the $y'$ axis, the magnetization will effectively be locked along this axis by the rf field. The spins are locked if the amplitude $\omega_1$ of the lock field is larger than the strength of the dipole-dipole couplings. In the rotating reference frame the magnetization experiences only the $B_1$ field and not the $B_0$ field when the rf is applied exactly on resonance. Efficient spin-locking requires that off-resonance effects are compensated, such as that all nuclei experience the same effective field. Therefore under spin-locking conditions the $B_1$-field plays the role of the static field in the rotating frame, which means that relaxation in the direction of $B_1$ (i.e. along the $y'$ axis depending on the phase of the spin-lock field) is similar to spin-lattice relaxation. The magnetization will relax to a zero equilibrium value with an exponential time constant $T_{1p}$ on the basis of the fact that the magnetic field in the rotating frame possesses a much smaller value than the static field ($T_{1p} >> T_2$) (for more details see [Blü]).

The situation is more complicated for the NMR-MOUSE®. The carrier frequency deviates from resonance because of the field inhomogeneities of the NMR-MOUSE®. Therefore the effective field is tilted toward the z-direction at angles $\theta$.
other than 90° (see Fig. 6.1). The angle $\theta$ and the amplitude of the effective field are given by

$$\tan \theta = \frac{B_1}{B_0 + \omega_{rf} / \gamma}, \quad [6.1]$$

and

$$B_{eff} = \sqrt{B_1^2 + (B_0 + \omega_{rf} / \gamma)^2} = -\gamma \omega_{eff} \quad [6.2]$$

respectively. The effective relaxation rate $(T_{1,\rho,eff})^{-1}$ is a combination of the longitudinal relaxation rate in the laboratory and in the rotating frame:

$$\frac{1}{T_{1,\rho,eff}} = \frac{1}{T_1} \cos^2 \theta + \frac{1}{T_{1,\rho}} \sin^2 \theta \quad [6.3]$$

![Diagram](image)

**Fig. 6.48** Magnetic fields in the rotating frame [Blü]. Depending on the offset of the NMR frequency from the rotation frequency $\omega_{rf}$ of the rotating frame, a fictitious magnetic field acts along the z-direction. The vector sum of $B_{fic}$ and the $B_1$ forms the effective field $B_{eff}$ around which the magnetization is rotating with the frequency $\omega_{eff}$.

The tilt angle becomes thus a function of the position in the sample. In the highly inhomogeneous fields of the NMR-MOUSE® we actually record an integrated value of the spin-lattice relaxation time in the rotating frame as a result of different relaxation times for each voxel of the sample. In the locking interval, spin-lattice
Integral dispersion of rotating frame spin-lattice relaxation time

relaxation is determined by effective angular frequencies \( \omega_{\text{eff}} = \omega_{\text{eff}}(\vec{r}) \) which are spatially distributed according to the field gradient. This integral can be performed numerically from a given distribution of the static and rf fields [Bal]. On the other hand, the frequency dependence of \( T_{1\rho} \) in combination with the highly inhomogeneous fields in which we handle results in an integrated dispersion of the \( T_{1\rho} \).

5.2 Pulse sequence and theoretical procedure

Through spin-locking of the magnetization along the direction of the effective field, the energy relaxation time in the rotating frame \( T_{1\rho} \) can be measured. For measuring the spin-lattice relaxation time in the rotating frame by the NMR-MOUSE\textsuperscript{®} in highly inhomogeneous fields we used a pulse sequence analogous to the LOSY (Lock Selective Spectroscopy) [Wies4]. With this technique [Rom1, Rom2] slice selection is performed by spin locking the magnetization after excitation by a 90° preparation pulse in the presence of a gradient of the external field \( B_0 \). In the case of the NMR-MOUSE\textsuperscript{®} the field has in a good approximation a quadratic profile [Blü], so that we can utilize this technique to test if a volume selection occurs.

The spin-locking efficiency is spatially restricted. If the amplitude of the spin-locking rf field is much greater than that of the local fields, that is

\[
B_{1i}^{(SL)} \gg B_{\text{loc}}
\]

any spin couplings other than inhomogeneous Zeeman interactions can be neglected. This case is named the liquid state limit. The solid-state limit is defined by

\[
B_{1i}^{(SL)} \approx B_{\text{loc}}
\]

In this case dipolar couplings are relevant during the spin-locking process. The effective fields during the rf pulses tend to be oriented in directions other than those of the rotating frame axis. Therefore transformations to the tilted rotating frame are necessary.

The pulse sequence for measuring the \( T_{1\rho} \) relaxation rate by the NMR-MOUSE\textsuperscript{®} is illustrated in Figure 6.2. The spin-lock effect is observable by the NMR-MOUSE\textsuperscript{®} despite the large resonance offsets and the strong variations of \( B_1 \) within the spatial coordinates [Gut1].
Fig. 6.49  Schematic representation of the pulse sequence used for measuring $T_{1\rho}$ with the NMR-MOUSE® at 20.1 MHz. It consists of a preparation pulse $\theta_x$ and a 90° phase-shifted spin-lock pulse (amplitude $B_{1\text{SL}}$). After a refocusing pulse $2\theta_y$ the signal intensity of the following echo was recorded as a function of the length of the spin-locking pulse, which was incremented after a waiting time $\tau_0$.

From the experimental point of view $T_{1\rho}$ is a very good parameter for the characterization of ultra slow molecular motion on the time scale of $\omega_i^{-1}$ (kHz region), because $\omega_i$ can be adjusted via the spin-lock power [Blü]. In principle, if we try a relaxation experiment in a smaller static field, to sample this slow regime of molecular motions, the sensitivity is poor because S/N is proportional to $B_0$. The $T_{1\rho}$ technique maintains the sensitivity of the high field measurement while probing relaxation in a low field regime.

6.3 Experimental

6.3.1 Samples
A series of differently cross-linked elastomer samples based on commercially available natural rubber (NR) SMR10 (Malaysia) was investigated. The additives were 3 phr (parts-per-hundred-rubber) ZnO and 2 phr stearic acid. The sulfur and accelerator contents are 1-1 phr for the sample NR1 and 5-5 phr for NR5. The accelerator is of the standard sulfenamide type (TBBS, benzothiazyl-2-tert-butylsulfenamide). After mixing the compounds in a laboratory mixer at 50°C, the samples were vulcanized at 160°C in a Monsanto MDR-2000-E vulcameter. The degree of cross-linking was measured by the low frequency shear modulus at a temperature of
$160^\circ$ C in the vulcameter directly after the vulcanization. The measurements were performed with an oscillation amplitude of $\pm 0.50^\circ$ and a frequency of 1.67 Hz.

**Table 6.1** Cross-link series of natural rubber.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sulphur-accelerator content (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR1</td>
<td>1-1</td>
</tr>
<tr>
<td>NR2</td>
<td>2-2</td>
</tr>
<tr>
<td>NR3</td>
<td>3-3</td>
</tr>
<tr>
<td>NR4</td>
<td>4-4</td>
</tr>
<tr>
<td>NR5</td>
<td>5-5</td>
</tr>
</tbody>
</table>

For the experiments performed under mechanical stress a simple home build stretching device was used. The natural rubber bands had dimensions of 180 mm x 35 mm x 4 mm in the unstrained state. The NMR-MOUSE® was positioned below the rubber band in contact with the surface of the rubber band. The width of the band was larger than the diameter of the radio-frequency coil of 13 mm.

### 6.3.2 NMR Experiments

The $^1$H NMR experiments in inhomogeneous fields were performed with a home made NMR-MOUSE® sensor equipped with a Bruker Minispec spectrometer operating at a carrier frequency of 20.1 MHz. The pulse length employed in all the measurements was $2.5 \mu$s (pulse attenuation 10 dB), and the recycling delay 1s for the rubber samples and 8 s for water. The decay curves for determining $T_{1p}$ were recorded using the pulse sequence from Fig. 6.2 by incrementing the spin lock time. $\tau_0$ was 0.5 ms, and the echo time $\tau = 0.2$ ms The spin-lock amplitude was constant at 20 dB, and 15 dB for the angle dependent measurements. The intensity of the signals for the spin lock pulse length of $\tau_{sl} = 0.8$ ms were measured for the NR1 band with $\lambda=2.6$ versus the angle $\Theta$ between the direction perpendicular to the magnet poles and the direction of the stretching force. These measurements can easily be performed with the NMR-MOUSE® sensor.
6.4 Results

6.4.1 Spin-lock time dependence on volume selection

The volume selection which appears by recording the spin-lattice relaxation decay in the rotating frame under strong field gradients is studied by the NMR-MOUSE® on a water sample [Wies4]. The liquid-state limit is valid because the dipolar couplings are averaged out by Brownian motion. The spin interactions which produce the local field in the tilted rotating frame are negligible against the spin locking field $B_1$.

In the inhomogeneous magnetic fields of the NMR-MOUSE® the excitation tip angle is 90° only in a couple of voxels in the sample, so that the total magnetization is transverse and can be spin-locked. The consequence is a residual component of the local magnetization immediately after the excitation pulse. During the spin-lock pulse the $z$ magnetization precess about the instantaneous effective field $B_{\text{eff}}$. These components are always perpendicular to the spin-locked magnetization and subject to transverse relaxation in the rotating frame and decay with the time constant $T_{2\rho}^*$.

$$\frac{M(\tau_{\text{SL}})}{M(0)} = \frac{1 + (G_z z / B_1)^2 \exp \left( -\frac{\tau_{\text{SL}}}{T_{2\rho}^*} \right)}{1 + (G_z z / B_1)^2}. \quad [6.6]$$

$G_z$ represents the field gradient in the $z$ direction. If $T_{2\rho}^* < < T_{1\rho}$ and $\tau_0 > T_{2\rho}^*$ no contribution to the acquired signal is expected and the spin-lattice relaxation experiment is not affected. Under such conditions the signal only depends on the ratio $G_z / B_1$ [Dem]:

$$\frac{M(\tau_{\text{SL}})}{M(0)} = \frac{1}{1 + (G_z z / B_1)^2}. \quad [6.7]$$

In Figure 6.3 we present the dependence of the signal intensity on the locking time by using the pulse sequence illustrated in Fig. 6.2. It is obvious that after the time interval at the beginning ($\tau_0 = 0.5$ ms) where the magnetization evolves around the effective field and decays with $T_{2\rho}^*$ (much shorter than $T_{1\rho}$), no volume selection is present.
Fig. 6.50 Dependence of the echo signal intensity on the duration of the spin lock pulse (Fig. 6.2) for $\tau_{\text{SL}} \gg \max[T_{2,\rho}^*]$ recorded with the NMR-MOUSE® on a water sample. The spin lock pulse length $\tau_{\text{SL}}$ was incremented for a fixed value of $\tau_0 = 0.05$ ms, and the echo time was $\tau = 0.2$ ms. The spin-lock amplitude was 20 dB.

6.4.2 The influence of the spin-lock field strength on volume selection

We expect a linear relationship of the excitation profile and the spin-lock rf amplitude for the solid state as well as for the liquid state limit [Dem] (see eq. [6.7]). For the natural rubber samples the measurements confirm our expectations (Fig. 6.4). If the lock pulse attenuation is higher (the rf amplitude is lower) the signal intensity is going down, that means that the selected volume of the sample is smaller. The water sample shows the same trend, but less accurate. The reason could be the oscillations we have at 0.8 ms by measuring the decay of the signal versus lock pulse length (compare Fig. 6.3).
6.4.3 The integrated dispersion of the $T_{1\rho}$ in different cross-linked elastomers

First of all we demonstrate the monoexponential decay of the spin lock behavior for three different cross-linked natural rubber samples. Here the spin couplings are relevant during the spin locking pulse. The local field is assumed to be produced by dipolar interactions between the nuclei, therefore a difference in the cross-link density of the elastomer sample should be easy to detect by the NMR-MOUSE®. We would actually expect a biexponential decay in elastomers. In our case it is possible that the solid like component disappears because of the long $\tau_\rho = 0.5$ ms and we detect only the liquid like part of the curve [Wies4].
Fig. 6.52  Monoexponential decay of the signal intensity measured with the pulse sequence of Fig. 6.2 by the NMR-MOUSE® for three different cross-linked natural rubber samples NR1, 3, 5 (see Tab. 6.1). The spin lock pulse length $\tau_{SL}$ was incremented for fixed value of $\tau_0 = 0.5$ ms, and the echo time was $\tau = 0.2$ ms. The spin-lock amplitude was 20 dB.

In Figure 6.6 the spin-lattice relaxation rate in the rotating frame is recorded versus cross-link density. A nonlinear dependence can be identified. This agrees with the transversal relaxation measurements done with the NMR-MOUSE® for a SBR cross-link series [Gut2].

In contrast to the laboratory frame, spin-lattice relaxation in the rotating frame is indicative of slow motions with rates in the frequency regime of $\omega_{\text{eff}} = \gamma B_{\text{eff}}$ defined by the spin-lock pulse amplitude. Molecular fluctuations in this range are also relevant for transverse relaxation. Therefore the $T_2$ and $T_{1p}$ relaxation curves should be similar.
6.4.4 The integrated dispersion of $T_{1\rho}$ on strained elastomers

The dependence of $T_{1\rho}^{-1}$ on the extension ratio $\lambda$ is not linear (Fig. 6.7). For $\lambda$ values larger than 1 the interchain dipolar interactions between $^1$H have to be taken into account. This was shown for the full width at half-height measured from SQ NMR spectra vs the extension ratio of a natural rubber band [Schn3]. The curves are very similar to those in the Fig. 6.8, where the transverse relaxation ratio is presented. At a value of $\lambda \approx 2.25$ there is a sharp bend indicating the stress induced crystallization. In the case of $T_{1\rho}$ after the sharp bend, the spin lattice relaxation rate remains roughly constant. This is because of the fact that both are related to the slow molecular motion, but in the case of $T_{1\rho}$ the dipolar couplings are reduced by half in the rotating reference frame [Kimm].
Fig. 6.54  Spin-lattice relaxation rate in the rotating frame as a function of the elongation ratio measured with the spin-lock pulse sequence (Fig. 6.2). The spin lock pulse length $\tau_{sl}$ was incremented for a fixed value of $\tau_0 = 0.5\,\text{ms}$, and the echo time $\tau = 0.2\,\text{ms}$. The spin-lock amplitude was 20 dB. Dotted lines are drawn through the points to indicate that the trends in the data differ for lower and larger values of the uniaxial extension.

Fig. 6.55  Transverse relaxation rate measured with a Hahn-echo pulse sequence by the NMR-MOUSE®. Dotted lines are drawn through the points to indicate that the trends in the data differ for lower and larger values of the uniaxial extension.
6.4.5 The anisotropy of $T_{1p}$

In ordered tissues the transverse relaxation rate $1/T_2$ is known to exhibit the “magic angle phenomenon” [Hak]. Due to the anisotropic structure of a strained elastomer the transverse relaxation rate shows an angular dependence on the square of the second Legendre polynomial $P_2(\cos \Theta)$, having a minimum for the magic angle [Hai]. This is related to the fact, that the residual dipolar and quadrupolar couplings depend on the angle between the direction of the static magnetic field $B_0$ and the direction of the applied uniaxial stretching force for elastomer materials [Call, Sot]. In the case of the NMR-MOUSE® because of the $B_0$ inhomogeneities an effective orientation angle ($\Theta$) can be defined between the direction of the applied force and the axis oriented perpendicular to the permanent magnet faces (z-direction).

The angular dependence of the transverse relaxation rate measured with the NMR-MOUSE® for a NR band with $\lambda = 2.6$ using a Hahn echo pulse sequence is shown in Fig. 6.9b). The dependence shows a broad minimum around an angle close to the magic angle of $\Theta_m = 54.7^0$. By recording the angular dependence of $T_{1p}$ as a function of the orientation angle with the NMR-MOUSE® under the same conditions a similar trend related to the square of the second Legendre polynomial is not observable (Fig. 6.9a). Although in our case the solid state limit dominates, where $B_{1(SL)} \approx B_{loc}$ and the spin couplings are relevant, the sensitivity of $T_{1p}$ rate does not exceed the margin of the error of the NMR-MOUSE® measurements. Let us compare the x-scale of both graphs in Fig. 6.9. A simple rough calculation of $\frac{x_{\text{max}} - x_{\text{min}}}{x_{\text{max}}} \times 100$, where $x_{\text{max}}$ and $x_{\text{min}}$ are the maximum and minimum value of the $T_{1p}$ and $T_2$ rates for Figs. 6.9a and b resp., result to 40 % for the $T_2$ curve, while for the $T_{1p}$ this value is just 10 %. This means that it is easier to show the angular dependence by the use of the $T_2$ measurements. Nevertheless, Fig. 6.10 shows the right dependence of the signal intensity for a fixed value of $\tau_{SL}$ as a function of the angle $\Theta$, although by repeating the calculation mentioned above we obtain a value of about 10%. This is obvious because by recording only one point of the decay the experimental conditions are more suitable (duration, temperature constancy, selected volume, evaluation etc.), so that the measurement is more accurate. In chapter 4, Figure 4.10 illustrates the angular dependence of the Hahn echo for a fixed echo time and is fully comparable with our results from the spin-lock experiment.
Fig. 6.56 a) Angular dependence of the spin-lattice relaxation rate in the rotating frame for the natural rubber sample NR1 with elongation ratio $\lambda=2.6$ measured by the NMR-MOUSE®. The angle between the direction of the uniaxial stress force and the axis perpendicular to the faces of the permanent magnet is denoted by $\Theta$. The $T_1 \rho$ decays have been recorded using the pulse sequence of Fig. 6.2 by incrementing the spin-locking time $\tau_{SL}$ for a fixed $\tau_0 = 0.5$ ms. Straight lines are drawn only as a guide for the eyes. b) Angular dependence of the transverse relaxation rate for the same natural rubber sample NR1 with elongation ratio $\lambda=2.6$ measured by the NMR-MOUSE®.

Fig. 6.57 Angular dependence of the echo intensity for the natural rubber sample NR1 with elongation ratio $\lambda=2.6$ measured by the NMR-MOUSE® with the pulse sequence of Fig. 6.2 by a fixed spin-locking time $\tau_{SL} = 0.8$ ms. The angle between the direction of the uniaxial stress force and the axis perpendicular to the faces of the permanent magnet is denoted by $\Theta$. 
6 Integral dispersion of rotating frame spin-lattice relaxation time
General conclusions and outlook

The general objectives of this work are related to the methodology of NMR in grossly inhomogeneous fields, especially of the NMR-MOUSE®, and its applications in the material science. New and traditional techniques have been developed and implemented for the NMR-MOUSE®, having as ultimate goal the enlargement of its range of applications. Moreover, with the aid of a mobile NMR sensor the newly introduced methods give access to new types of information, like the segmental orientation and the slow motion of polymer chains in cross-linked elastomers. The final aim is to correlate the respective NMR parameters with the structural and viscoelastic properties of the respective polymer.

High resolution NMR has become a standard method for chemical analysis in industry. Nevertheless, the possibility to use a mobile magnet to scan over an object otherwise inaccessible to NMR becomes more and more important. As a price for the practical advantages of such device where the sample is placed outside the magnets for acquiring magnetic resonance information, we have to fight with the accompanying handicap, the spatial inhomogeneities of the magnetic fields.

The results of the investigations can be summarized as follows:

1. An attempt was made to detect high resolution spectra in elastomers by the NMR-MOUSE®. In principle this is feasible, using a train of Hahn echoes, which gives a signal encoded by homonuclear dipolar couplings, but not by field inhomogeneities and heteronuclear dipolar couplings. The polymeric system considered in the context of this work comprised fluorinated elastomers. Unfortunately the intergroup homonuclear dipolar couplings were too strong so that a Pake doublet could not be resolved. This effect was also evident from measurements performed in homogeneous high magnetic fields. Furthermore in the situation of the NMR-MOUSE® measurements, the strong field
inhomogeneities are not fully refocused by the radio-frequency pulses. In the low, inhomogeneous magnetic fields it would be suitable to take an oriented sample, like a stretched elastomer or fiber. In this case the dipolar couplings are more pronounced but at the same time the \( T_2 \) becomes shorter and difficult to record with the NMR-MOUSE\textsuperscript{®}. An improved NMR-MOUSE\textsuperscript{®} with much shorter dead-time and without any background signal would be a remedy.

2. Multipolar spin states like, dipolar encoded LM, DQ coherences and dipolar order were excited and detected for the first time in strongly inhomogeneous magnetic fields [Wies2]. Suitable pulse sequences were developed for filtering individual multipolar spin states after simultaneous excitation caused by the inhomogeneous fields. A new method for detection of \(^1\text{H} \) DQ filtered signals using the decay curves with improved signal-to-noise ratio was developed suitable for the NMR-MOUSE\textsuperscript{®} [Wies1]. The residual dipolar couplings are affected by the cross-link density, as well as by local strain. This fact was evidenced in the context of this work using the NMR-MOUSE\textsuperscript{®}. To validate the method and the results obtained in inhomogeneous fields, we additionally performed the measurement in homogeneous magnetic fields.

Moreover, the anisotropy of the local strain, which affects the chain orientation was measured by multipolar spin states in stretched elastomers. In soft samples with a macroscopic induced orientation of the segments, the transverse relaxation is anisotropic, the dipolar interactions follow the molecular orientation. For large samples the use of single-sided NMR is recommendable, since the measuring device can be rotated with respect to the object. As an additional promising future application, the possibility to map the space distribution of the strain in elastomers was investigated for the first time using the NMR-MOUSE\textsuperscript{®}. The use of residual couplings of protons as a physical quantity sensitive to the segmental orientation in the presence of a heterogeneous strain distribution in elastomers extends the field of applications of the NMR-MOUSE\textsuperscript{®}. The main challenge of the DQ signals is related to perform chain orientation measurements even in the presence of liquids, whose contribution to the acquired signal is minimized.

3. A further method for characterizing the segmental order in elastomers, based on residual van Vleck moments was implemented [Wies3]. First of all, the possibility to excite and detect a magic echo in grossly inhomogeneous magnetic
fields was shown. The important feature of the magic echo is that it refocuses the single-quantum coherence evolution for a complex network of dipolar coupled nuclei. Moreover, the combination of the magic with the Hahn echo, namely the mixed echo is not sensitive to the inhomogeneities of the $B_0$ magnetic field. The theory introduced shows, that under accordion like changes (expanding and compressing) of the magic sandwich, the residual van Vleck moments can be determined for a dipolar network in elastomers. The signal should be free from the disturbance of the transverse relaxation and $B_0$ magnetic field inhomogeneities.

The results presented are preliminary, a more detailed analysis in homogeneous, as well in inhomogeneous fields is required. In contrast to the method of multipolar spin states this method has the advantage that the signal-to-noise ratio is larger and the measurement time is much shorter.

4. The structure/properties relation in elastomers can be elucidated by measuring the slow motions of the polymer chains. A procedure to measure spin-lattice relaxation times in the rotating frame was investigated using the NMR-MOUSE® [Wies4]. This procedure is able to avoid the delicate problem of volume selection present for the spin-lock sequence. Therefore, the access to quantitative values of $T_1$ is given. The effect of cross-link density and elongation was analysed, as well as the anisotropy of chains in stretched elastomers.

Summarizing, the results of this work will extend the range of applications of the mobile NMR sensor by providing qualitative and quantitative information about elastomers under various conditions. We extended the panoply of NMR parameters that can be used with the NMR-MOUSE® for establishing structure-property relations in materials. Moreover, there are promising perspectives for the characterization of tissue order in connective tissues, muscles and blood vessels with the aid of the NMR-MOUSE®.
8 References


Appendix

New pulse programs

A1. double_q_xy.app

# pulse sequence #

count = 0;
while(tau < tau_end)
mark(-1,1,0);
pulses;
    sd(get_rdl*1000);
    ssp(pl,ph90,att1); #90x#
    ssp(tau-pl/1000);
    ssp(pl,ph18,att2); #180-x#
    ssp(tau-pl/1000);
    ssp(pl,ph90,att1); #90x#
    sd(0.5*t1-pl/1000);
    ssp(pl,ph90,att1); #90y#
    sd(tau-pl/1000);
    ssp(pl,ph17,att2); #180-y#
    sd(tau-pl/1000);
    ssp(pl,ph90,att1); #90y#
    sd(0-t-pl/1000);
    ssp(pl,ph88,att1);
    sd(tau-1-pl/1000);
    ssp(pl,ph16,att2);
    sd(tau-1-acq/2+2/1000);
    cta;
    adi(acq,acq*1500,phrc);
endpulses;

#arrays for phase cycling#

ph90[0]=0; ph18[0]= 180; ph17[0] = 270; ph89[0] = 90; ph88 [0] = 0; ph16[0] = 90; phrc[0]= 90;
A2. double_q_max_xy.app

```c
# pulse sequence #

count = 0;  
while(tau < tau_end)  
mark(-1,1,0);  
pulses;  
sd(get_rd*1000);  
ssp(pl,ph90,att1); #90x#  
sd(tau_max-pl/1000);  
ssp(pl,ph18,att2); #180-x#  
sd(tau_max-pl/1000);  
ssp(pl,ph90,att1); #90x#  
sd(0.5*t1-pl/1000);  
ssp(pl,ph17,att2); #180-y#  
sd(tau_max-tau-pl/1000);  
ssp(pl,ph17,att2); #180-y#  
sd(tau-pl/1000);  
ssp(pl,ph89,att1); #90y#  
sd(t0-pl/1000);  
ssp(pl,ph88,att1);  
sd(tau1-t-pl/1000);  
ssp(pl,ph16,att2);  
sd(tau1-acq/2+2/1000);  
cta;  
ad(acq,60,phrc);  
endpulses;

#arrays for phase cycling#

ph90[0]=0; ph18[0]= 180; ph17[0] = 270; ph89[0] =  90; ph88[0] =  0; ph16[0] = 90; phrc[0]=  90;  
```
A3. dip_ord_yz.app

```c
# pulse sequence 

count = 0;
while(tau < tau_end)
mark(-1,1,0);
pulses;
    sd(get_rd*1000);
    ssp(pl,ph90,att1); #90x#
    sd(tau-pl/1000);
    ssp(pl,ph18,att2); #180-x#
    sd(tau-pl/1000);
    ssp(pl,ph91,att3); #45y#
    sd(0.5*11-pl/1000);
    ssp(pl,ph17,att2); #180-x#
    sd(tau-pl/1000);
    ssp(pl,ph92,att3); #45y#
    sd(tau-pl/1000);
    ssp(pl,ph17,att2); #180-x#
    sd(tau-acq/2+2/1000);
    cta;
    adi(acq,acq*1000,phrc);
endpulses;
```

#arrays for phase cycling#

```c
ph90[ 0] =  0; ph90a[ 0] = 90; phi[ 0] = 180;
ph90b[ 0] = 270; phrc[ 0] = 90;
```

A4. magic_echo.app

```c
# pulse sequence 

count = 0;
while(tau < tau_end)
mark(-1,1,0);
pulses;
    sd(get_rd*1000);
    ssp(pl,ph90,att1); #90x#
    sd(tau-pl/1000);
    ssp(pl,ph18,att2); #180-x#
    sd(tau-pl/1000);
    ssp(pl,ph91,att3); #45y#
    sd(0.5*11-pl/1000);
    ssp(pl,ph17,att2); #180-x#
    sd(tau-pl/1000);
    ssp(pl,ph92,att3); #45y#
    sd(tau-pl/1000);
    ssp(pl,ph17,att2); #180-x#
    sd(tau-acq/2+2/1000);
    cta;
    adi(acq,acq*1000,phrc);
endpulses;
```
A5. mixed_echo_acordeon.app

```
# pulse sequence #

count = 0;
while(tau > tau_end)
    mark(-1,1,0);
pulses;
    sd(get_rd*1000);
    ssp(pl,ph90,att1);
    sd(0.3-tau-pl/1000);
    ssp(pl,ph90a,att1);
    ssp(1000*tau,ph90,att2);
    ssp(pl,ph90b,att1);
    sd(0.3-tau-acq/2+2/1000);
    cta;
    adi(acq,acq*1000,phrc);
endpulses;

#arrays for phase cycling#
ph90[ 0] =  0; ph90a[ 0] = 90; phl[ 0] = 180;
ph90b[ 0] =  90; phrc[ 0] = 90;
ph90b[ 3] = 0; phrc[ 3] = 0;
```

A6. spin_lock_new.app

```
# pulse sequence #

count = 0;
while(tauSL < tau_endSL)
    mark(-1,1,0);
pulses;
    sd(get_rd*1000);
    ssp(pl,ph90,10);
    ssp(tauSL*1000,ph18,attSL);
    sd(tau-pl/1000);
    ssp(pl,ph90b,att1);
    sd(0.3-tau-acq/2+2/1000);
    cta;
    adi(acq,acq*1000,phrc);
endpulses;

#arrays for phase cycling#
ph90[ 0]=  0; ph18[ 0]=  0;phrc[ 0]= 90;
ph90[ 1]=  90;ph18[ 1]=  0;phrc[ 1]= 180; # x y y #
ph90[ 3] = 270;ph18[ 3]=  0;phrc[ 3] = 0; # y x x #
```
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